SEDIMENTS ON THE CONTINENTAL MARGIN OFF THE WEST COAST OF SOUTH AFRICA

G.F. BIRCH

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ABSTRACT

A general study of the composition and texture of sediments off the west coast of South Africa has been supplemented by more detailed investigations of the clay fraction (<2μm sediment) and of the extensive glauconite and phosphorite deposits.

Sediments on the continental shelf, which narrows (100 to 30 n. miles) and deepens (300 to 500 m) towards the south, form rough belts parallel to the coast. Most coarse sediment is confined to the littoral zone and Holocene mud is concentrated at the base of a rocky nearshore platform. A veneer of Quaternary quartzitic sand seawards of the Recent mud belt wedges out onto a Tertiary erosion surface on the mid shelf. Residual glauconite and phosphorite sands derived by erosion during Tertiary sea level fluctuations cover large parts of the mid shelf in the south. Most of the slope and parts of the outer shelf in the north are draped by Recent foraminiferal and coccolithophorid debris.

Although no latitudinal variations in the geochemistry and mineralogy of the fine fraction is apparent, clear seaward trends are evident. Illite is richest close to the coast (>80%); kaolinite is most abundant on the outer shelf (20%), and slope sediments contain the highest concentrations of montmorillonite (30%). Minor chlorite is sometimes present (<5%). Al, K and Mn are most abundant in the source rocks and river sediments of the hinterland, and on the continental margin their abundance decreases markedly seawards. Mn is readily desorbed on entering the sea, but most of the Fe, Al and K is contained in the detrital fraction. Ca, Ni, Zn and possibly Pb are more abundant in the marine clays than in the onland sediments. Ca is derived by the breakdown of calcareous organisms and Ni, Zn and possibly Pb are probably concentrated by biogenous processes in regions of upwelling and high biolcgical activity.

Onland, erosion of quartzitic phosphorites has resulted in extensive pelletal deposits. Similar phosphorite occurrences on the outer shelf are a southerly extension of the richer pelletal deposits off South West Africa. Quartzitic phosphorites have formed in nearshore areas of intense surface upwelling during transgressive and regressive periods. The accumulation and decay of siliceous phytoplankton in these regions has resulted in anaerobic bottom conditions and interstitial apatite precipitation. The calcareous and glauconitic phosphorites which cover extensive areas of the shelf have formed in regions of less intense subsurface upwelling. Here the input of P into the bottom sediment has been sufficient to cause replacement of calcareous mud and lithification of the upper sedimentary layer. The ubiquitous

presence of finely divided glauconite in the matrix of phosphorites and in foraminiferal tests is explained by co-replacement of clay minerals and micrite. Migration of deposition belts during changes in sea level has resulted in a heterogeneous mixture of phosphorite components and conglomeratic textures are produced by inclusion of limestone fragments in the bottom sediment.

Microprobe analyses indicate that glauconite is rich in K_2O (9,01%) and MgO (5,45%). Fe is probably emplaced in the glauconite structure independantly and prior to the fixation of K and it is possible that some of the Mg is located in the interlayer position. Most of the "glauconite" is composed of a mixture of apatite and glauconite minerals. Inclusion of quartz and calcareous material in some glauconite and mixed mineral pellets mitigates against a colloidal aggregation theory for their origin. Instead, evidence is presented which indicates that some glauconite and mixed pellets are derived from in situ alteration of bottom sediment and/or by glauconitization subsequent to fragmentation of the bedrock and formation of the pellet.

Holocene clay in glauconite-rich sediment contains insufficient Fe for present-day glauconite diagenesis. The reason for this is unclear, but it may be due to reduced upwelling and curtailed biogenic deposition. The concomitant reduction in the influx of P would also account for the absence of modern-day phosphatization. Phosphorites formed during the U. Eocene and M. Miocene and glauconite diagenesis occurred during M. Miocene/L. Miocene times.

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LIST OF CONTENTS

LIST OF FIGURES

Figures in the Appendix

LIST OF TABLES

LIST OF PLATES (all following page 210)

CHAPTER I. INTRODUCTION

1.1. The Joint Geological Survey/University of Cape Town continental margin project

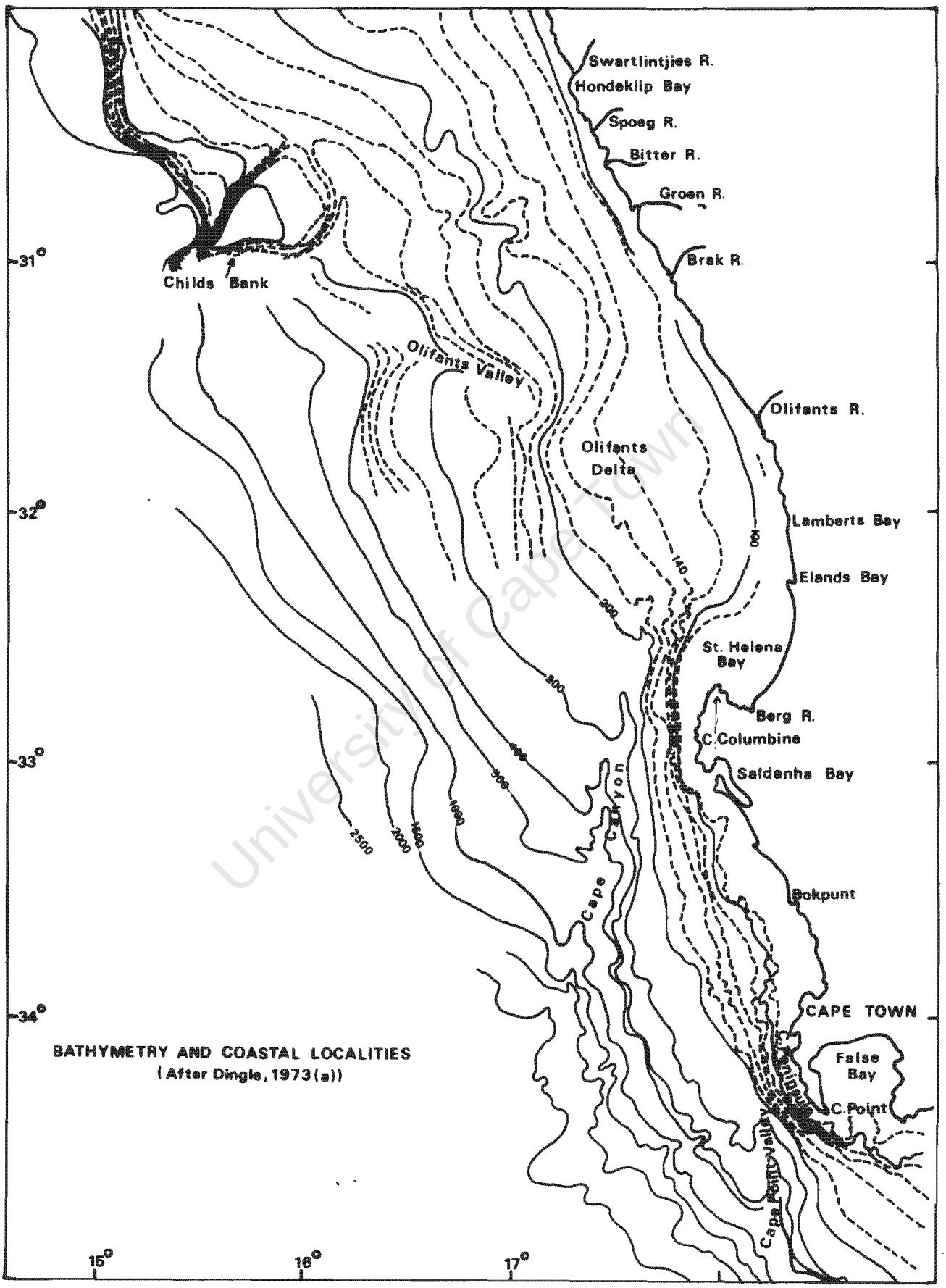
The continental margin project was initiated in 1967 by the South African National Committee for Oceanographic Research (SANCOR), but since 1972 the Marine Geology Programme has become a joint undertaking of the Geological Survey, Department of Mines, and the University of Cape Town. The main aims of the programme are to undertake a thorough geological survey of the continental shelf, slope and rise off the Republic of South Africa and South West Africa, and to establish the distribution, composition and origin of the marine glauconite and phosphorite deposits.

The preliminary survey of the area between the Angolan border in the west and Mozambique to the east has now been completed. For convenience the continental margin was divided into five regions for general sedimentological research: Agulhas Bank (Rogers, 1971); East Coast (Moir, 1975); western Cape shelf (this work); Orange-Lüderitz shelf (Rogers, in prep(a)) and Walvis-Kunene shelf (Bremner, in prep.). Specialized mineralogical and geochemical investigations of glauconite (Birch, 1971), phosphorite (Parker, 1971) and carbonate minerals (Siesser, 1971) have also been conducted on the sediment from various parts of the margin. The writer joined the Marine Geology Unit in 1972 with the purpose of studying the surficial sediments on the western Cape shelf.

1.2. Study area

The 509 off-shore samples (Appendix I) used in this study were recovered from the continental shelf and the upper slope off the west coast of South Africa between 30 and 35 degrees south, and 14 and 19 degrees east, an area of approximately 30 000 n. miles^2. In the following chapters this off-shore area is informally referred to as the "Western Cape Shelf" or simply as the region off the "Cape west coast".

Most sampling was done on a 10 n. mile grid pattern extending from the coast to depths of 1 500 to 2 000 metres, but in areas of special interest, for example the Cape Canyon and the nearshore region, the sampling interval was reduced. Sediment was collected from the research vessel THOMAS B. DAVIE of the University of Cape Town using a modified Van Veen grab in the shoaler parts of the shelf (approximately 200 metres) and a short (2 metre) gravity corer in the deeper regions (Fig.I-1). This equipment provided mixed sediment from a maximum depth of approximately 0,5 metres and samples were stored wet and unfrozen in plastic containers. Rocks were recovered by dredging. During the initial stages of the project, navigation was by radar inshore and by means of dead reckoning and celestial fixes off shore, but more recently



BATHYMETRY AND COASTAL LOCALITIES
(After Dingle, 1973(a))

Figure I-2

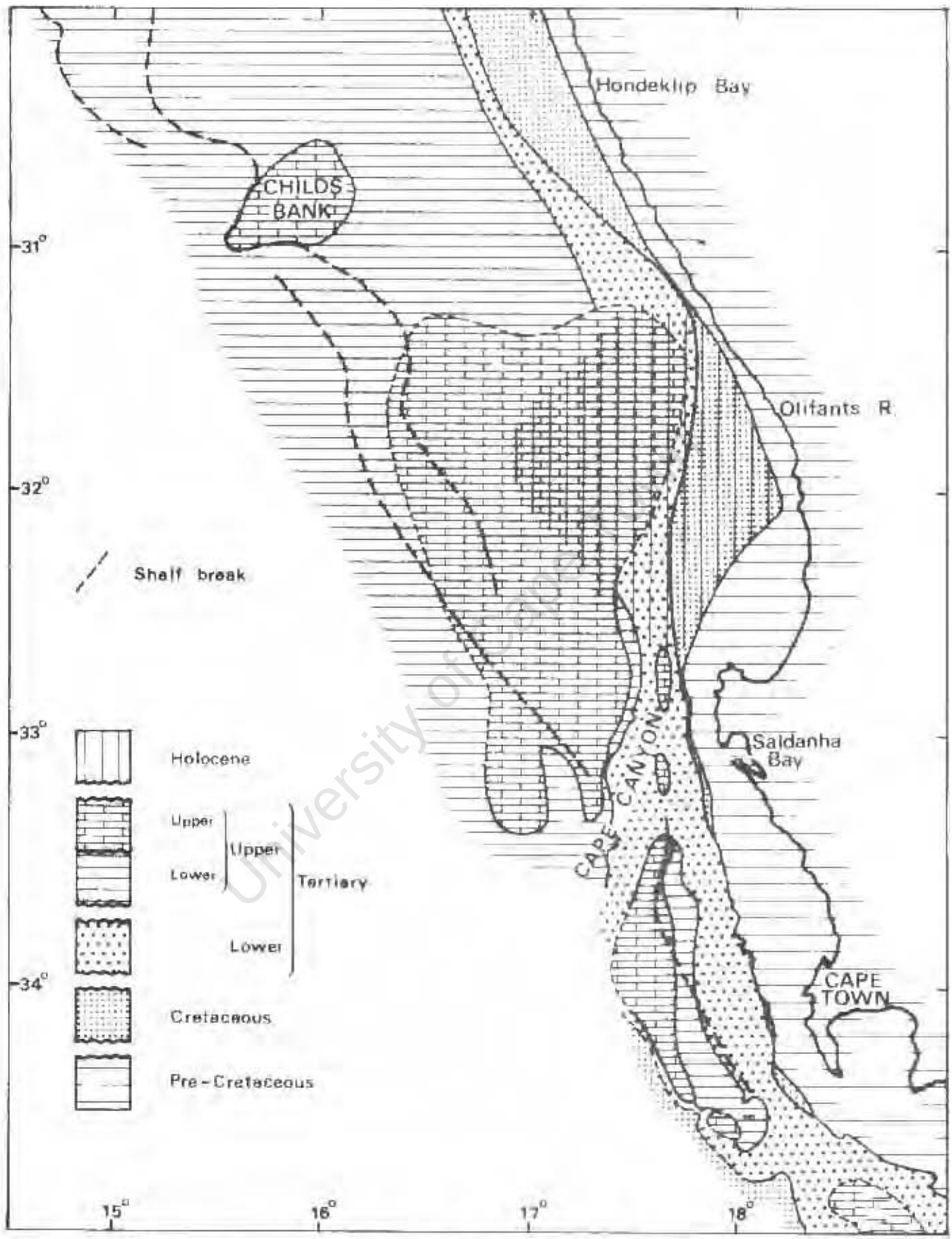
navigation has been improved by acquisition of the DECCA navigational system.

The overall width of the shelf is determined mainly by the configuration of the coastline, as the edge of the continental shelf maintains a north west strike throughout the area (Fig.I-2). The shelf is both wide and deep in relation to the worldwide average (47 n. miles and 130 metres, respectively, Shepard, 1963). It is narrowest (31 n. miles) west of the Cape Peninsula and Saldanha Bay and widest off the Olifants River (100 n. miles) and west of Cape Agulhas (130 n. miles). A double shelf break at about 300 metres and 550 metres occurs in the north near the Childs Bank, and a normal, well-developed shelf edge is found at approximately 400 metres off the Cape Peninsula. The break shallows southwards to about 350 metres west of Cape Agulhas. A low gradient slope of 1,267 degrees off Hondeklip Bay steepens markedly to 2,917 degrees west of the Cape Peninsula in the south (world average is 4,238°, Shepard, 1963).

Several large topographic features occur on the margin. Childs Bank is a flat-topped plateau at about 200 metres depth at the edge of the shelf off Hondeklip Bay. It has a steep, slump-generated slope face with a gentle landward edge and is separated from the inner shelf by a depression about 70 metres deep (Dingle,1973(a)). The Cape Canyon (Simpson and Forder, 1968 and Dingle, 1971) cuts obliquely across the shelf and the slope west of Saldanha Bay. The canyon has steep walls with a maximum relief of approximately 800 metres and is virtually free of Quaternary sediments. The Cape Canyon and the Olifants River Valley, which crosses the shelf to the north, are buried on the mid shelf by Quaternary sediments of the Olifants River Delta, but both features emanate from the vicinity of the Olifants and the Berg Rivers. Another minor valley, the Cape Point Valley, cuts diagonally across the shelf south of the Cape Peninsula and can be traced to a depth of about 2 000 metres.

Beneath the shelf a sedimentary wedge composed of a seaward-thickening Cretaceous and Tertiary units unconformably overlies the quartzite shales and metasediments of the Lower Palaeozoic basement (Dingle, 1971 and 1973(a)).Cretaceous strata form a narrow outcrop (about 20 n. miles) seaward of a nearshore basement cliff north of Saldanha Bay, whereas to the south only intermittent outcrops up to 1,5 n. miles wide are evident. Cretaceous sediment also outcrops on the slope south of the Cape Canyon and once on the canyon floor (Fig.I-3). During the Cretaceous, the continental margin underwent rapid upbuilding and outbuilding onto a subsiding basement, but since this time the rate of sedimentation has decreased and outbuilding has become more important (Dingle, 1973 (a)).

Three major Tertiary transgressions have been identified by Dingle (1971). These occurred in the early Tertiary (Palaeocene/Eocene); mid Tertiary



Geology of the Continental Margin

(After Dingle, 1971 and 1973[a])

Figure I-1

(Miocene) and late Tertiary (Pliocene). Palaeogene sediments are mainly glauconitic clays and limestones and a thin shallow-water facies, composed of both glauconitic and phosphatic limestones and sandstones, was laid down during the Miocene and Pliocene (Siesser et al., 1974). The uppermost Tertiary sediments were subjected to vigorous erosion, probably sub-aerially, during the major Late Tertiary regression, and now occur only as isolated outliers west of Hondeklip Bay (the Childs Bank) and off Saldanha Bay and the Cape Peninsula (Dingle, 1973 (a)).

The continental margin can be subdivided into three distinct morphological zones: a narrow nearshore rocky platform, a gently-shoaling, wide shelf with subdued relief, and a smooth, steeply-graded slope (Fig.I-4).

The nearshore rocky platform is narrow (3-5 n. miles) north of the Olifants River and off Cape Columbine, but it widens to 20 n. miles off St. Helena Bay and west of Cape Town and Cape Agulhas. The platform is bounded by a steep seaward edge, the base of which deepens from approximately 90 metres west of Hondeklip Bay to about 150 metres off the Cape Peninsula (Dingle, 1971). The edge of the platform extends in a straight line south of Cape Columbine until it turns abruptly landwards for 7 n. miles west of the Fish Hoek fault. It appears that the platform was down-faulted in a manner similar to that on the adjacent landmass. Hollows on the inshore margin of the platform are filled or partially filled with sediment. The platform comprises pre-Cretaceous basement, the composition of which can sometimes be deduced from the rocks recovered by dredging (Fig.I-4). Acoustically-transparent mud up to 15 metres thick (Du Plessis, pers.comm.) extends along the base of the rocky platform between Elands and Hondeklip Bays and south of False Bay. The surface of this fine sediment is composed mainly of faecal pellets(Plate I-2).

A continuous sediment cover on the inner shelf has resulted in a generally smooth, subdued relief, whereas the outer shelf consists essentially of a rocky erosion surface with a patchy residual cover. The slope and parts of the outer shelf in the north are smooth because of a thick mantle of sediment. West of Lamberts Bay is an anomalous region where terrigenous detritus covers the entire shelf width. V-shaped valleys, 300 to 400 metres wide, at the shelf edge in this region are probably the heads of slump nicks (Plate I-1).

1.3. The hinterland

Gneisses, schists and granites of the Namaqualand metamorphic complex lie to the north of the Olifants River mouth and sandstones, quartzites, carbonates and shales of the Nama, Cape and Karoo Groups and Supergroups comprise the landmass to the south. Lower Palaeozoic quartzites of the Cape Supergroup have been intruded by late Precambrian granites and a thin veneer of unconsolidated Quaternary sediments covers most of the coastal margin.

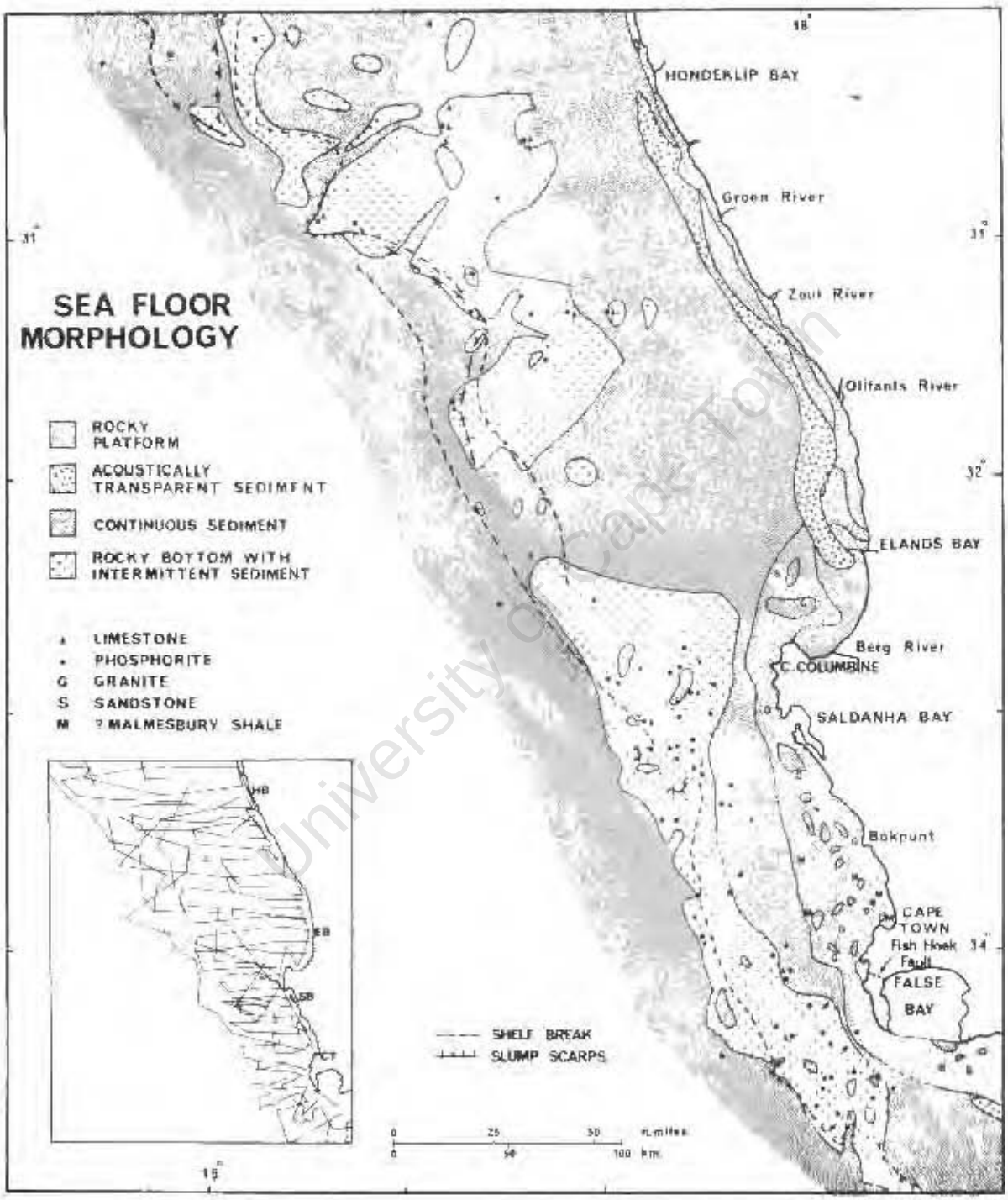


Figure I-4

The southern region has a Mediterranean-type climate of moderately low (40 cm/yr) precipitation and the remaining parts of the catchment area are semi-arid (10-20 cm/yr)(Schulze, 1965). A large drainage area of approximately 25 000 kilometres^2 north of Saldanha Bay, lies adjacent to a broad (100 n. miles) shelf region, whereas to the south the shelf narrows to 25 n. miles and the catchment area is small. The combined drainage area of the Berg and the Olifants Rivers (46 064 and 5 098 kilometres^2, Midgley and Pitman, 1969) constitutes more than half the adjacent onland region, and because these rivers drain the most mountainous areas of the wetter south, they are the only perennial rivers on the west coast of South Africa, excluding the Orange River to the north. Although no statistics on sediment discharge are available, both the fact that relatively large quantities of water are released by these rivers (Berg River, 1 973 568 m^3/yr; Olifants River 6 973 568 m^3/yr, Midgley and Pitman, 1969), and the fact that they drain mainly the argillaceous sediments of the Karoo, Cape and Nama Groups and Supergroups, strongly suggest that these rivers are the major source of sediment reaching the coast. Large quantities of sediment on the shelf seawards of these rivers supports this assumption and indicates that they were probably the most important sediment source in pre-Holocene times as well.

1.4. Hydrology and meteorology

A combination of hydrological and meteorological factors has produced two independent current systems, one in deep oceanic water and the other over the continental shelf (Bang, 1971; and 1973(a) and (b) and 1974).

The South Atlantic High Pressure Cell is encircled by a belt of South East Trade Winds which drive the saline, warm waters of the South East Trade Wind Drift northwards up the eastern Atlantic Ocean (see Fig.VIII-3 in Birch, Rogers and Bremner, 1973). The northward-moving water within the zone of upwelling over the continental shelf is termed the Benguela Current (Hart and Currie, 1960; Shannon, 1966 and Bang, 1971 and 1973(a)). This current is divided into an off-shore divergence belt of subsurface upwelling over the shelf break, which separates the oceanic current system from the less saline, cooler and more nutrient-rich upwelled water on the shelf, and an inshore region of spasmodic and discontinuous surface upwelling. Southward-flowing bottom countercurrents have been predicted from dynamic calculations for the upper slope and at the base of the rocky nearshore platform (Hart and Currie, 1960; Stander, 1964 and O'Brien and Hurlburt, 1972).

Upwelling in the inshore zone is variable owing to short and long term variations in wind-stress, which is the main driving force (Bang, 1973(a)). Owing to wind-stress variability and to varying orientation of the shoreline, upwelling is intensified in cells centred on certain points, such as the Cape Peninsula and north of Cape Columbine (Bang, 1973(b)). A marked seasonal variation in

the wind direction also has a significant effect on upwelling. In summer (November to February), the prevailing south east trade winds blow strongly off shore producing intense upwelling, but in winter when the passage of westerly depressions moves north, the wind changes to north west. Upwelled cells therefore expand and contract in the short term, but usually expand progressively as the summer upwelling season advances (Bang, 1973(a)). Periodic calms during the summer months and reversals in wind direction in the equinoxes, cause marked variations in the nutrient content of the water. Such changes in the food supply result in mass mortalities of plankton and fish in the nearshore regions (Andrews, 1974). The high input of organic matter to the bottom sediments and its bacterial and chemical decomposition deplete the bottom water of oxygen and lead to anaerobic conditions (De Decker, 1970).

Hydrological surveys made over a 10-year period show oxygen-depleted water (<2 ml/l) in the nearshore region to depths of approximately 130 metres (De Decker, 1970). Occasionally oxygen values of 0 mg/l are reported (De Decker, 1970) for a continuous nearshore zone from St. Helena Bay to Walvis Bay, 1 000 kilometres to the north. All oxygen values below 1 mg/l determined by De Decker (1970) fell within the temperature range 8,9 to 9,6°C and the salinity of this water was likewise restricted to between 34,65 and 34,75°/oo. No areal distribution for phosphate concentration in sea water is available, but figures produced by De Decker (1970) show that water containing <1 mg/l O_2 frequently has up to 3 microgram atoms per litre phosphorous. De Decker has also noted a close relationship between the trend of the oligoxic water (<2 mg/l O_2) and the abundance of zoo- and phytoplankton.

1.5. This investigation

Three fields of research are covered in this investigation. A general survey of the total unconsolidated sediment is followed by more specific studies on the fine fraction (<2μm) and of the glauconite and phosphate components. Each topic is discussed fully in the relevant chapters, and the main conclusions drawn from the studies are summarized in the final chapter.

At the commencement of this project little was known of the sediments off the south west African coast, and therefore the present investigation represents primarily a reconnaissance survey (Emery, 1969, has classified this region as "poorly known"). Because a thorough knowledge of components is a pre-requisite to an understanding of processes and products, a detailed examination of the surficial sediments is a fundamental objective of this investigation. The texture, geochemistry and mineralogy of the total sediment are therefore discussed first. In the absence of quantitative data on currents and sediment movement on the shelf, elucidation of sedimentary processes has been limited to inferences based on the nature and distribution of the bottom

sediment. An attempt has nevertheless been made to correlate textural and compositional data to Tertiary tectonics, Pleistocene sea-level fluctuations and Holocene sedimentation.

Upwelling is a well-recognised phenomenon off this coast, but its imprint on the modern bottom sediments has not been determined. As clay minerals are sensitive indicators of environmental conditions, a geochemical and mineralogical investigation of the fine fraction (<2μm) is the subject of considerable interest. The data have been discussed in terms of diagenesis, provenance and dispersal. These aspects are considered in Chapter III.

Upwelling also has obvious implications in the genesis of authigenic minerals, and this has led to a detailed study of glauconite and phosphorite which constitute major components of these sediments. In view of the potential use of these minerals in agriculture (Overall, 1968(a) and (b)) and in industry (Skow, 1961, in McRae, 1972) and because of the feasibility of extracting rare elements such as uranium, fluorine and rare earths from phosphorites (see Tooms et al., 1969), these deposits are of more than purely academic interest. The distribution, nature and origin of these minerals are discussed in Chapter IV.

With the exception of the initial overall reconnaissance survey, studies of individual mineral phases have been carried out in preference to investigations of the bulk sediment. More meaningful data have been obtained by determining the geochemistry of the clay minerals rather than that of the total sediment, and likewise, microprobe studies of the glauconite and phosphate minerals have been more profitable than detailed major and trace element analyses of the bulk rock.

Mr. J.P. Willis, of the Geochemistry Department, University of Cape Town, pioneered the micro-analytical techniques used in the study. He also made some of the initial determinations of the glauconite and apatite minerals. All other work discussed in this thesis is that of the writer, except where specified.

References pertinent to the various topics considered in this investigation are presented in the relevant chapters.

CHAPTER II. SEDIMENT TEXTURE AND MINERALOGY

2.1. Introduction

Knowledge of sediment texture and composition is a pre-requisite to the understanding of sedimentary processes. The regional sedimentary pattern has been investigated to determine the origin of terrigenous detritus on the continental margin. In addition, it is important to establish the imprint of upwelling on the bottom sediments in order to elucidate the authigenic and biogenic processes, which have given rise to the considerable glauconite, phosphorite and carbonate deposits.

A map of sediment composition around South Africa was compiled by Nekritz and Busch (1969) using bottom-type Admiralty charts. These qualitative data were superseded by several studies, mostly Russian, of the sediments on the south-west African continental margin. Investigations by Fuller et al. (1965), Emelyanov and Senin (1969), Senin (1970), Bezrukov and Senin (1971), Emelyanov (1971) and Gershanovich et al. (1972) have established some of the sedimentological provinces on the shelf.

In broad outline the regional sedimentary pattern is as follows: depressions on the pre-Cretaceous coastal platform are partially filled by shelly quartzitic sands, and mud, typically rich in faecal pellets, has accumulated at the base of the cliff at the seaward edge of the platform. Fine sediment becomes less abundant towards the mid shelf where quartzitic muddy sands predominate. The rocky mid and outer shelves are mantled in the north by a discontinuous veneer of foraminiferal sand and in the south by phosphatic and glauconitic sediment. Foraminiferal mud covers the slope.

In this chapter the textural aspects of the sediment are considered first, after which the composition of the biogenic, authigenic and terrigenous fractions is assessed. Finally, the sedimentary history of the region is discussed.

2.2. Analytical methods

The techniques used in obtaining the data discussed in this chapter are described in detail in Appendix II. Only a summary of the procedures is presented below.

The gravel, sand, silt and clay contents of the sediment were determined on salt-free samples by wet sieving using 2mm and 63μm screens and by standard pipette methods. Sodium hexametaphosphate was employed as a deflocculent.

Calcium carbonate determinations were made gasometrically (Hülsemann, 1966). Because the CO_2 content of the carbonate fluorapatite mineral (francolite) in the sediment varies regionally, and as its contribution is minor (maximum error is 3 to 4% $CaCO_3$), the $CaCO_3$ values reported in this chapter have not been corrected for the presence of francolite.

The organic carbon content of the sediment was determined by a standard technique using wet-oxidation of the sample by hot chromic acid followed by titration of excess acid against ferrous sulphate (Morgans, 1956).

Sub-samples of all sediment recovered were sent to Phosphate Development Corporation, Transvaal for routine determinations of K_2O and P_2O_5. P_2O_5 analyses were carried out spectrophotometrically using an ammonium vanadate-molybdate method and K_2O determinations were made by X-ray fluorescence spectrometry.

An estimate of the faecal pellet content was made by soaking the sand fraction overnight in warm sodium hypochlorite followed by gentle ultrasonic disaggregation. The faecal pellet content was determined from the weight loss after wet sieving a second time and drying. Ultrasonic treatment also disaggregated non-faecal pellet material, and values, especially of calcareous sediment, are likely to be in error (see Appendix II-A(v) for details).

Glauconite was separated from the sediment using Franz Isodynamic electromagnetic separator by methods described by Birch (1971). However, as the glauconite pellets are commonly composed of an intergrowth of apatite and glauconite minerals (see Chapter IV), K_2O determinations were also made to estimate the distribution of this mineral phase better.

2.3. Sediment texture

2.3.1. Introduction.

The sediment on the continental margin off the Cape west coast is composed of a mixture of biogenic, authigenic and terrigenous materials which may be either modern, residual or relict. These surficial sediments are therefore not exclusively a product of modern conditions, but have formed in a variety of environments at different times. The use of the granulometric data for the interpretation of sedimentary processes is thus highly problematical. As a result, size studies have been restricted to fundamental gravel/sand/silt/clay determinations and to a coarse fraction (<63μm) analysis, at half phi intervals, of 241 selected samples.

2.3.2. Clay and silt.

Clay-size material (<4μm) is most abundant on the inner shelf north of Saldanha Bay (Fig.II-1) and on the outer shelf and slope, whereas the mid shelf is notably depleted in fine sediment. Clay values vary from greater than 50% near the coast off the Olifants River to less than 10% on the mid shelf. Although the distribution of silt closely follows that of the clay, only the mud on the outer shelf and upper slope is dominated by silt(Fig.II-1).

Large quantities of mud (silt plus clay) are aggregated into sand-size sediment by the digestive processes of polychaete worms. Disaggregation of the faecal pellets gives an estimate of the true mud concentration and also of

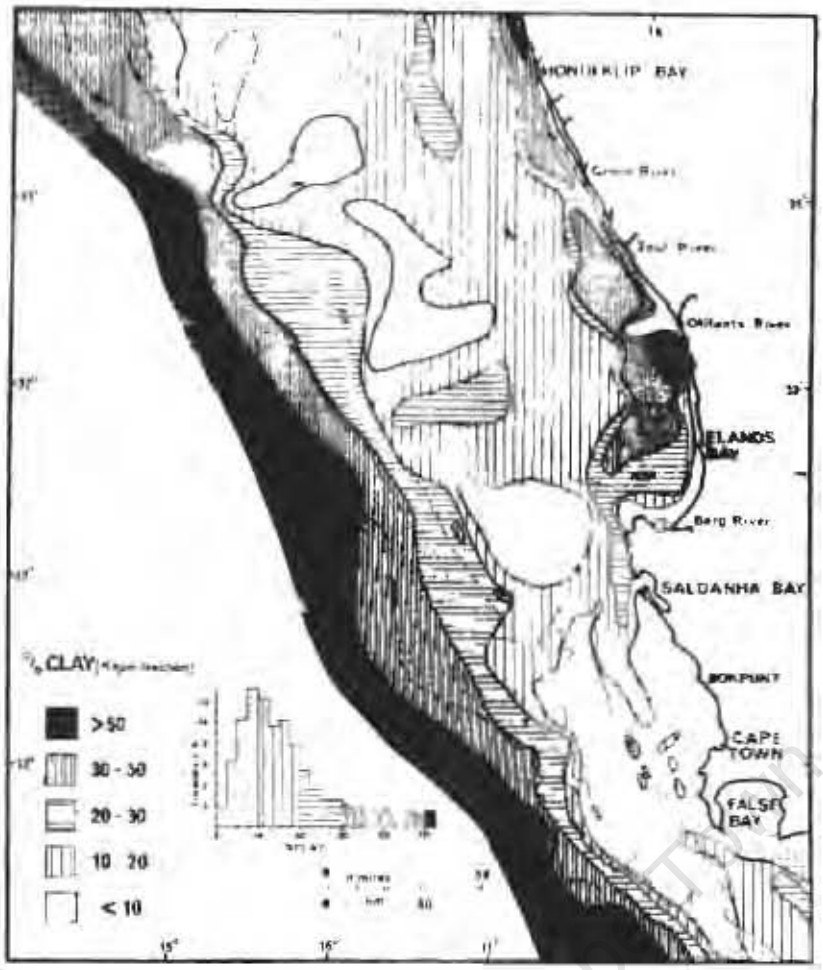
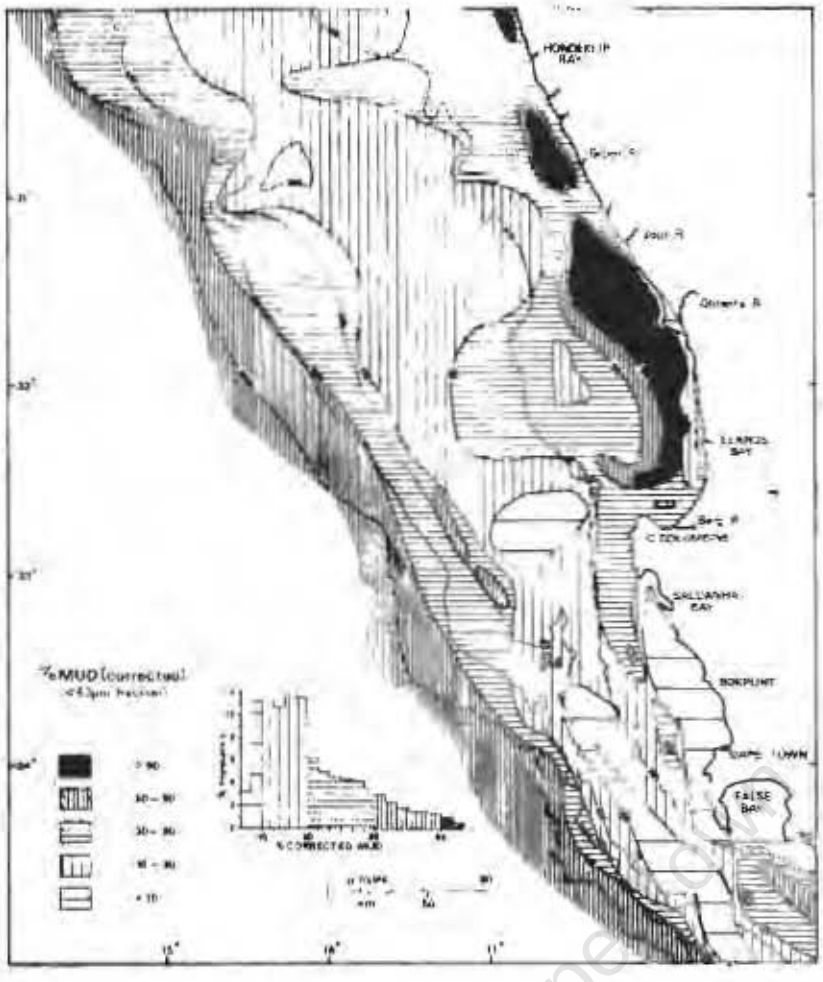


Figure II-1



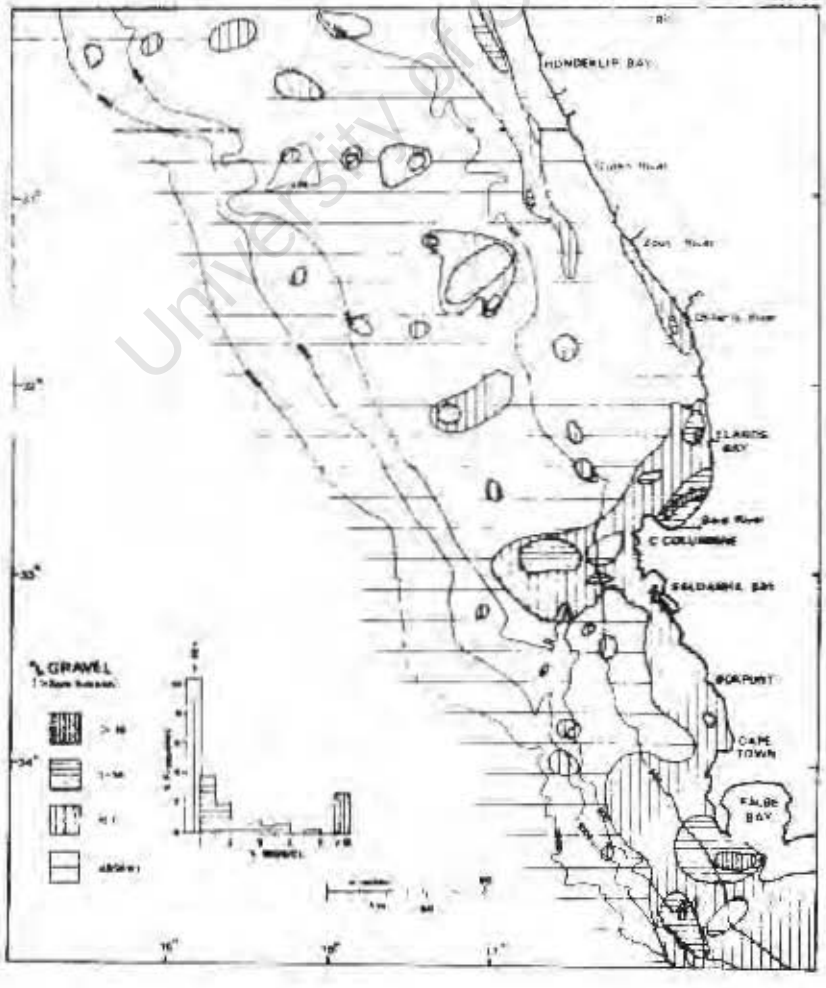


Figure II-2

the extent of the polychaete worm activity (section 2.4.3.). Mud values are greatly increased when the faecal pellet component is regarded as fine sediment. On this basis mud values between the Berg River and Hondeklip Bay are greatly increased (>90%) and the inner shelf throughout the region is characterized by muddy sediment (Fig.II-2).

2.3.3. Sand and gravel.

The mid shelf north of Saldanha Bay and most of the shelf to the south is mantled by sandy sediment (∿75% sand).

The gravel content is generally low (<10%), but small areas of gravelly sands occur in St. Helena Bay and south of Cape Point (Fig.II-2). Phosphorite and limestone gravel derived from underlying strata is most abundant on the mid shelf off Saldanha Bay and Cape Town. Quartz pebbles from the nearshore region between Hondeklip Bay and Zout River are probably eroded from Cretaceous outcrops, whereas similar deposits west of the Cape Peninsula and off Saldanha Bay are either weathered from the Cretaceous or from the Cape Granite basement. Numerous fragments of (?)Malmesbury shale and granite have been recovered from St. Helena Bay and from the inner shelf north of Cape Town, and bryozoan gravels have been found in the vicinity of Childs Bank and south west of Cape Point.

2.3.4. The sand-size fraction (63µm to 2mm).

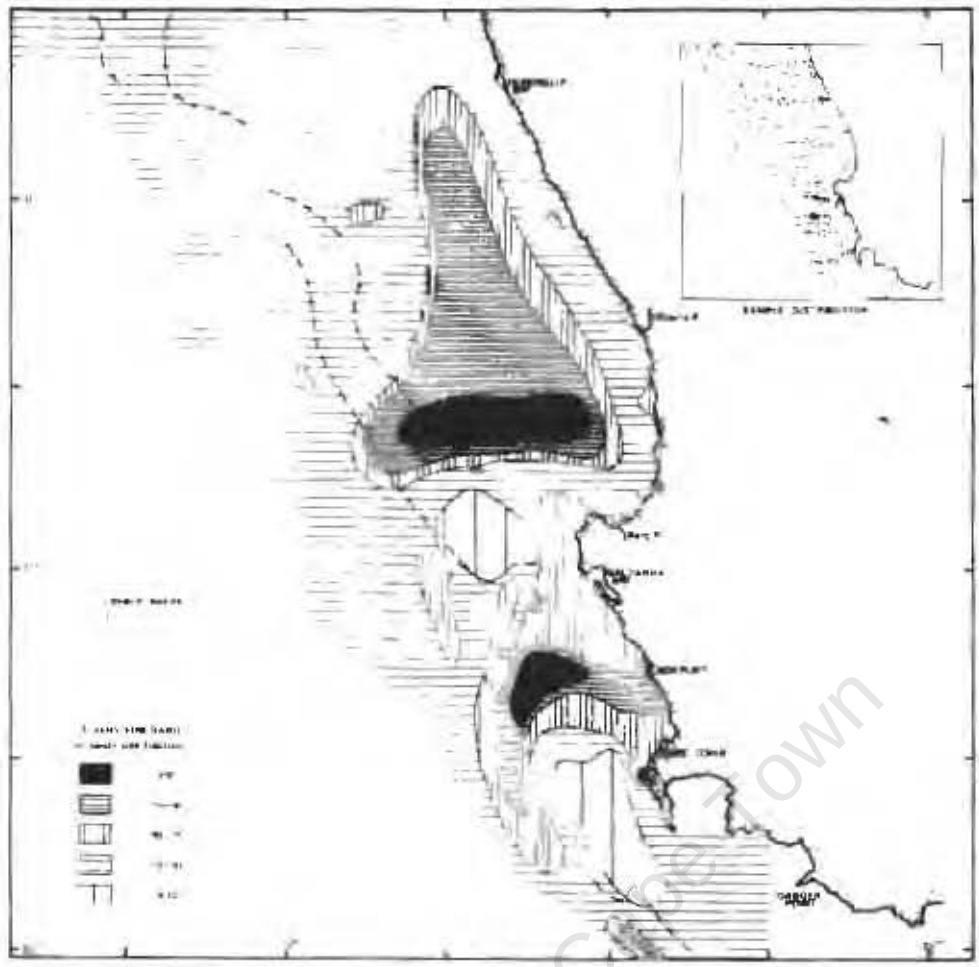
Although the sediments mantling the shelf have a varied origin, the size distribution of the coarse fraction portrays fairly faithfully the occurrence of the terrigenous, biogenic and authigenic components mentioned earlier. The regional distribution of sand is presented in Figures II-3 and 4 and only a very brief description of the salient features is mentioned below. The significance of the textural distributions will become more apparent when they are related to the compositional data in the following sections.

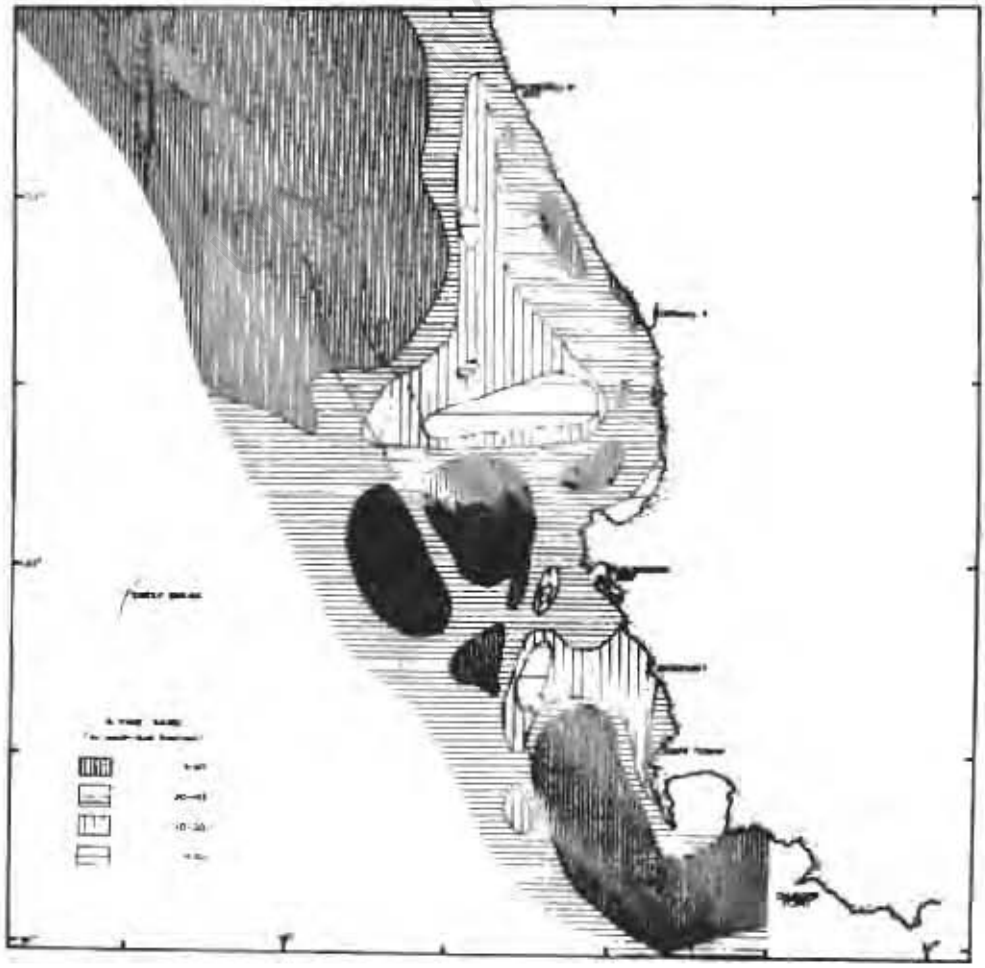
Very fine sand constitutes a large proportion of the coarse (>63µm) sediment on the mid shelf off the Olifants River and between Saldanha Bay and Cape Town, but the shelf sediments immediately adjacent to these localities are characterized by medium sands. The deeper regions of the margin north of the Olifants River are predominantly covered by fine sands, but large quantities (>20%) of coarse and very coarse sediment are restricted to a narrow belt along the inner shelf off Hondeklip Bay. Small deposits of coarse sediment also occur off the Berg River, west of Saldanha Bay and off the Cape Peninsula.

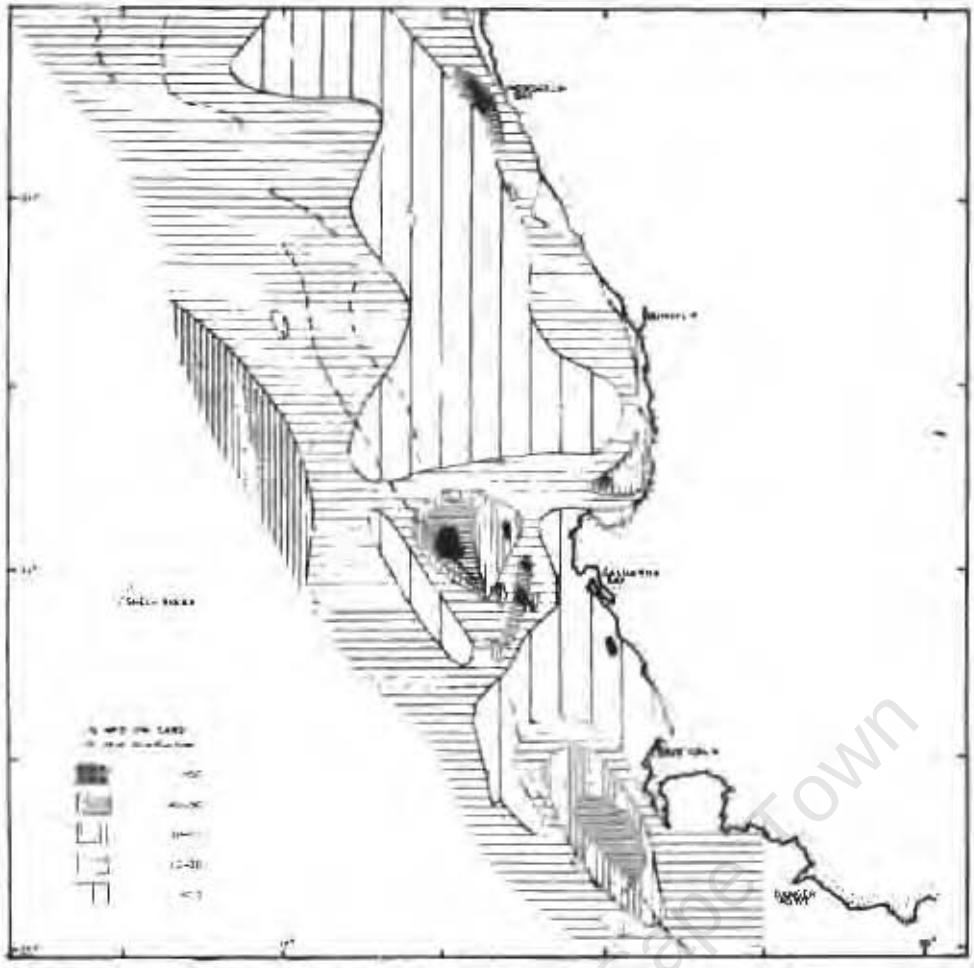
2.4. The biogenic fraction

2.4.1. Introduction.

The most important biogenic contribution to the outer shelf sediment is undoubtedly that of the calcareous flora and fauna, mainly planktonic and benthonic foraminifera, whereas the nearshore sediments have been extensively modified by polychaete worms. Generally the sediment becomes more calcareous







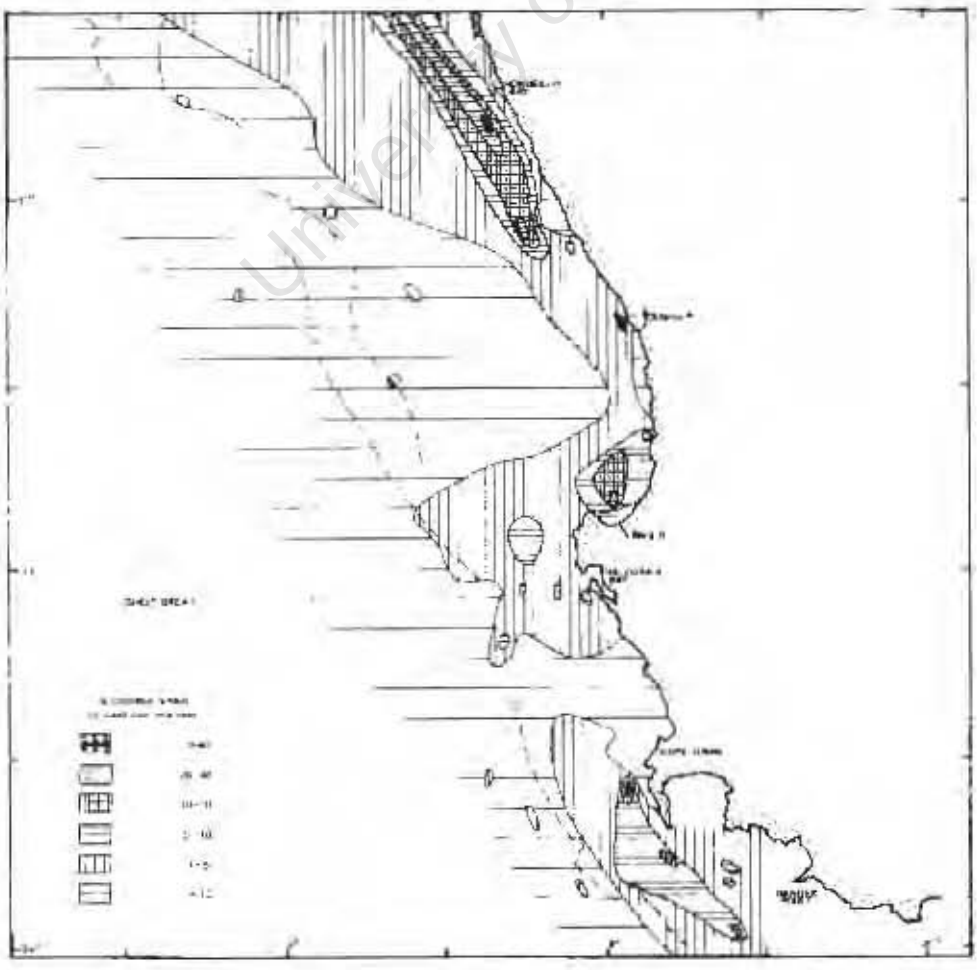


Figure II-4

seawards and values of up to 95% $CaCO_3$ have been recorded for slope sediment, but the average calcium carbonate content of the samples recovered is 33%.

A detailed investigation of the benthic foraminifera is presently being carried out in this department (Martin, 1974) and planktonic varieties have been studied by Siesser (1974) and Rogers (1974). The distribution of a number of foraminiferal species, which have been found to be characteristic of various sedimentary types, is discussed in section 2.4.3.

The extent of the biogenic activity on the shelf can be gauged by the high average organic carbon content of the sediment (1,68%) in relation to the mean value for continental shelves (0,5% C_{org}, Emery, 1960) The organic carbon content varies between 0,1 and 7,3%. Although the source of the organic matter is related to the upwelling of nutrient-rich water and high biological activity, the presence of abundant plant fragments in the sediments at the mouth of the Olifants River indicates that some organic matter is being derived from the continent.

The nature and distribution of the organic component is discussed in more detail below.

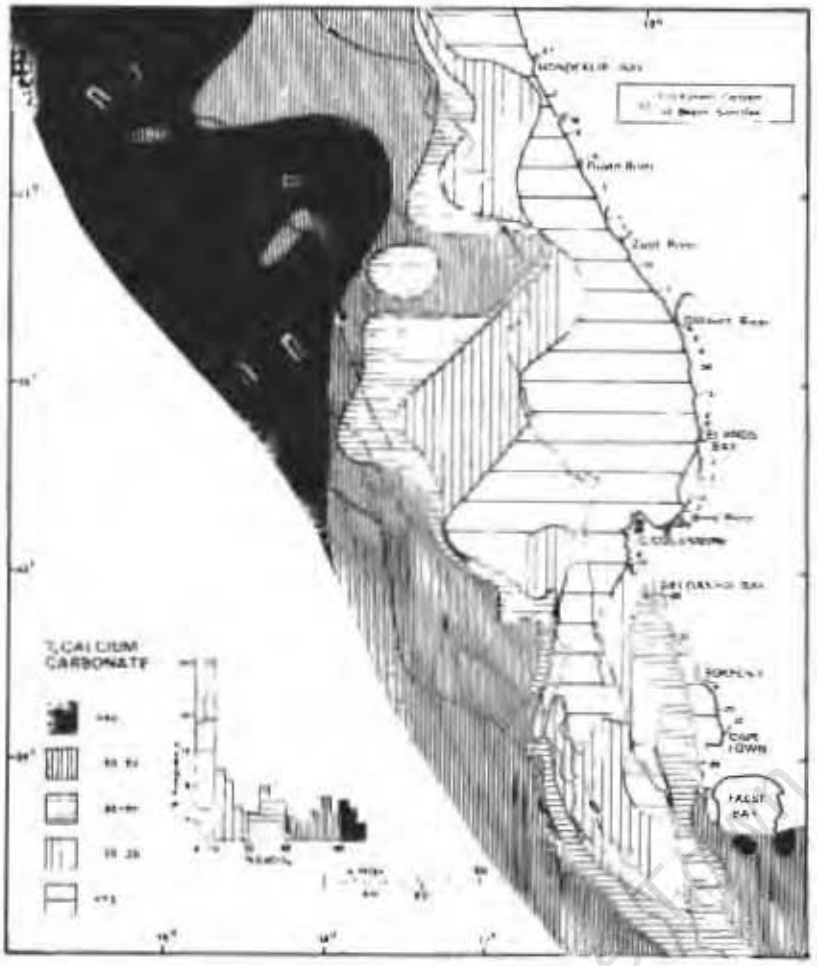
2.4.2. Calcium carbonate and organic carbon.

The carbonate distribution north and south of Saldanha Bay is markedly dissimilar. The shelf south of Saldanha Bay is relatively carbonate-poor (<30% $CaCO_3$), whereas to the north sediments containing more than 50% calcium carbonate extend onto the mid shelf. It is interesting to note (Fig.II-5) that west of Cape Town the 50% carbonate isopleth coincides with the 2000 metre isobath, but off the Olifants River it cuts diagonally across the shelf so that in the north it lies in the vicinity of the 200 metre isobath and within 30-40 kilometres of the coast. Calcareous sediments also dominate most of the continental margin south of False Bay.

Mineralogical and textural data have been combined to determine the nature of the carbonate phase of the fine sediment (Birch, 1973, Fig.VIIIA-9). As can be expected the distribution of calcareous muds (50% $CaCO_3$) follows very closely the occurrence of calcium carbonate in the total sediment. The non-calcareous nature of the total sediment west of the Olifants River and on the shelf south of Saldanha Bay is also reflected in the composition of the fine sediment in these regions.

Beach samples south of the Berg River are more calcareous (average 39% $CaCO_3$) than those to the north which contain only an average of less than 10% calcium carbonate. This is possibly due to higher terrigenous sedimentation in that region.

Sediments containing more than 5% organic carbon are located on the inner shelf between the Berg and Zout Rivers, but a discontinuous concentration of moderately enriched sediment (2,0% C_{org}) also occurs along the upper slope



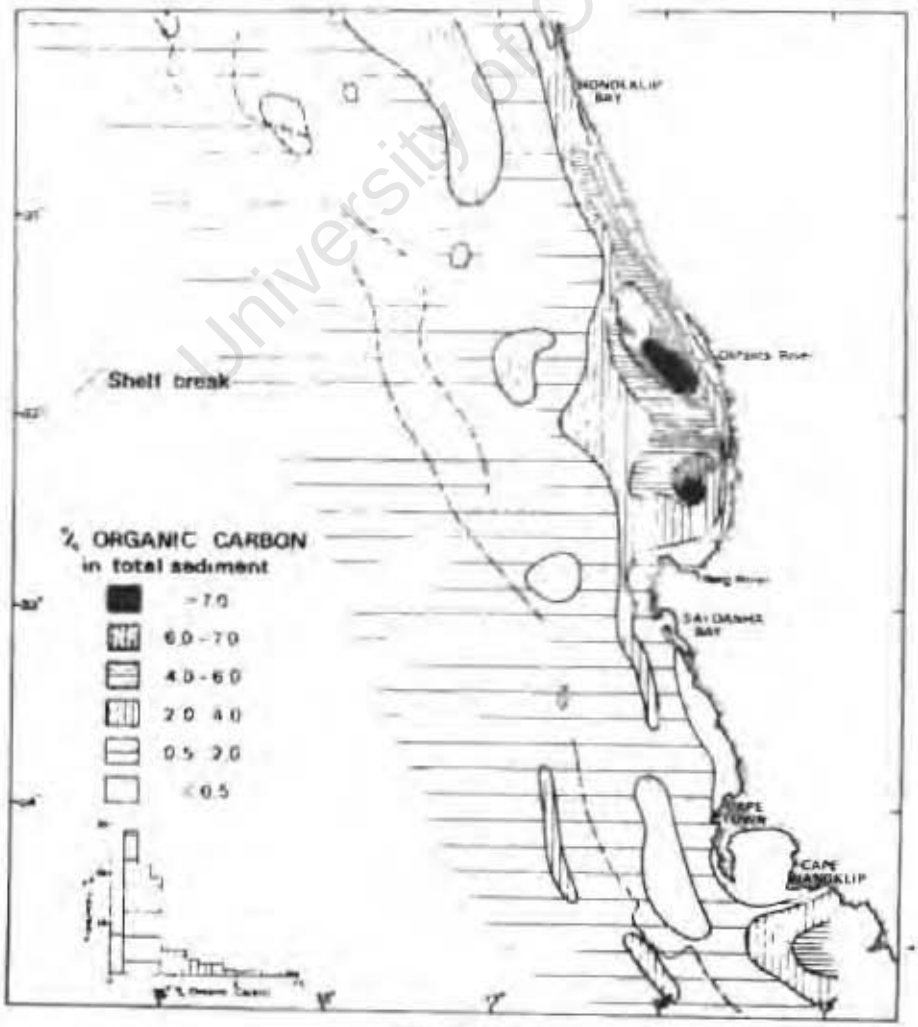


Figure II-5

(Fig.II-5). Sediments containing less than 0,5% organic carbon are found in only a few areas which are located in the nearshore and mid shelf regions south of Saldanha Bay.

Organic matter is being supplied to the shelf by rivers and by accumulation of marine organisms on the sea floor in areas of upwelling and biological activity. In order to assess the importance of these processes the distribution of organic carbon has been considered by removing the diluting effect of carbonate sedimentation (Birch, 1973, Fig.VIII-A-10). On a carbonate-free basis an extensive deposit of richly organic sediment (up to 15% C_{org}) is discernible on the outer shelf and upper slope north of the Olifants River, but the nearshore regions remain virtually unchanged. This could imply that the deposition of organic matter in the nearshore sediment was subservient to that occurring on the outer shelf. However, organic matter is also being diluted by nearshore terrigenous influx, and as the absolute rate organic deposition cannot be readily assessed, the validity of such an assumption remains doubtful.

The strong upwelling cell located between the Berg and Olifants Rivers (Shannon, 1966 and Bang, 1971) has resulted in high biological activity (Clowes, 1954) and an enrichment of organic matter in the bottom sediments ($\sim$7% C_{org}). The organic component is being retained in the sediment owing to the ability of clay minerals to adsorb readily organic matter from the sea water and to the rapid burial of sediment which effectively screens the organic material from the oxygenated overlying waters. The existence of an eddy current in St. Helena Bay (Duncan and Nell, 1969) and of generally quiet water conditions in this nearshore region, would, in contrast to the current-swept mid shelf, favour the deposition of finely disseminated organic matter. Oxygenation of the bottom sediment would be less vigorous in a quieter environment as well. Organic matter formed by biogenic process is being supplemented by the influx of organic debris from rivers entering the sea in this region. Faecal pellets are absent and organic values are low immediately off the Olifants River mouth, because burial has been too rapid for adsorption of organic particles by clay minerals and for the survival of polychaete worms (Fig.II-17). Rogers (pers.comm.) has noted a similar phenomenon off the Orange River to the north.

The combination of these factors has favoured the accumulation of organic matter in this region rather than in the 'open' shelf. Nevertheless, the mid shelf is generally enriched approximately four-fold in relation to normal shelf sediments (Emery, 1960) by the accumulation of large quantities of biogenic material, mainly planktonic foraminifera. The importance of this organic component will be discussed in Chapter IV.

2.4.3. Biogenic components.

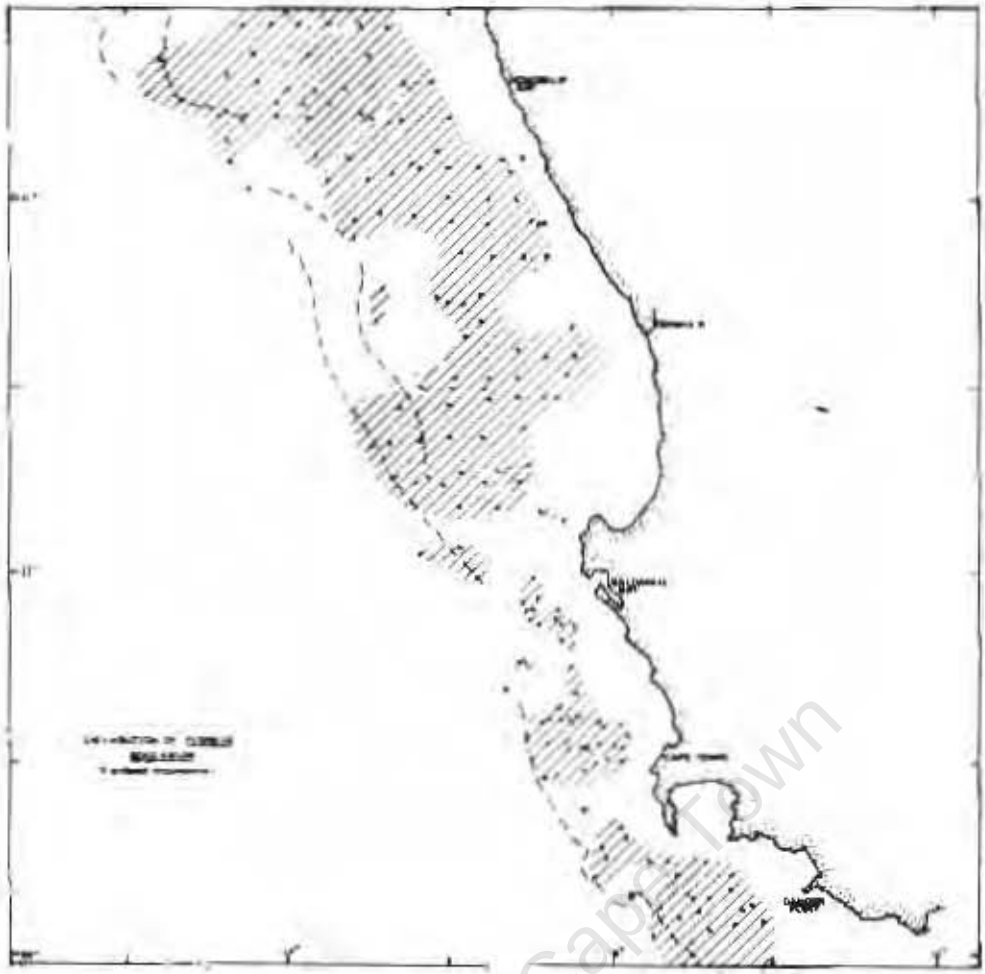
In a preliminary appraisal of dead and living benthic foraminifera in the sediment off the west coast of southern Africa, Martin (1974) suggested that the continental margin could be separated into five depth zones, each characterized by different faunal assemblages. However, depth involves a variety of environmental parameters which may in themselves limit distribution of foraminifera. These may include food supply, oxygen, salinity, pressure and currents. The occurrence of any particular species is dependent on all these factors, and if any is unfavourable the species will not survive. Studies indicate that zones established in one area on the basis of a faunal assemblage may only be applicable to an adjacent region if the environmental conditions are exactly the same (Murray, 1973). In the present study the occurrence of many planktonic and benthic fauna was noted in the hope that they would typify depth or some environmental aspect, such as sediment type, areas of upwelling etc. The distribution of fauna and flora which appear to concentrate preferentially under certain conditions is described below.

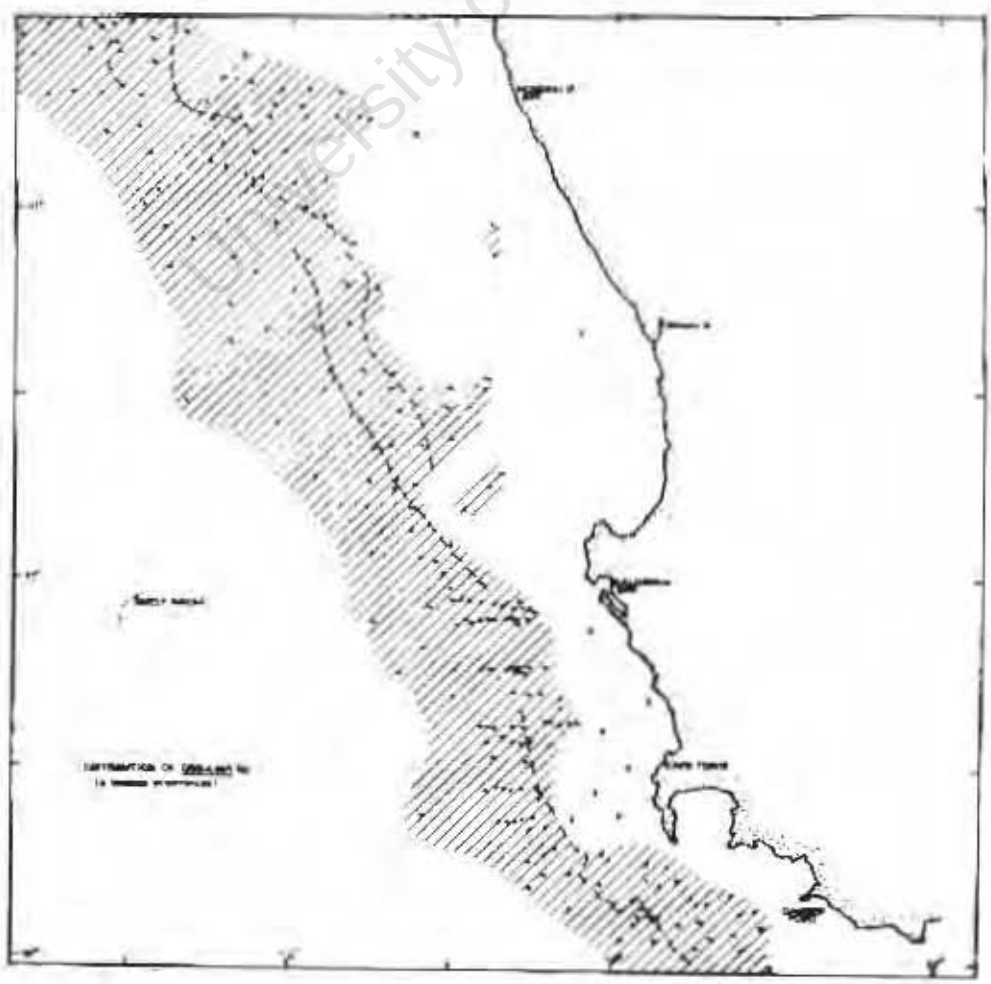
(a) Calcareous planktonic and benthonic foraminifera.

Ammonia beccarii Linné, Elphidium crispum Linné, E. cf. Macellum Fichtel and Moll, and Quinqueloculina seminulum Linné occur on the inner shelf (Fig.II-6) and are included by Martin (1974) in her zones 1 and 2 ie. about 120 metres depth. Although they are all present on the inner shelf they are most abundant in markedly different sediment types. Ammonia beccarii occurs in large numbers in the faecal pellet muds north of Cape Town, especially between the Berg and Zout Rivers, and also south of Cape Point, whereas Quinqueloculina seminulum and Elphidium spp. are found in pure quartzitic sands. Only off the Berg River do these two benthics inhabit muddy sediment and this could be due to the continuously changing conditions at the river mouth. Ammonia beccarii is also present on the slope west of Saldanha Bay and on the mid shelf west of Hondeklip Bay, but test preservation indicates that they are possibly reworked or transported faunas (Martin, 1974). These distributions correlate well with the findings of Phleger (1952; in Murray, 1973, p.124) who demonstrated that Elphidium spp. was related to a sandy sea floor and Haplophragmoids bradyi was restricted to muddy sediment in the nearshore region off Portsmouth, New Hampshire. Phleger (1956; in Murray, 1973, p.139) also found Ammonia beccarii to be restricted to the depth range 8-35 metres off the Texas central shelf.

Florilus boueanum d'Orbigny is present in the foraminiferal and glauconitic sands of the mid shelf (Fig.II-7) and is absent from the nearshore and slope muds. Martin (1974) has found this species to be most abundant in the depth range 109 to 122 metres.

Figure II-6





Although isolated occurrences of Orbulina universa d'Orbigny are present on the mid shelf and even in the nearshore (Fig.II-7), large numbers of this species only exist in the region of the shelf break and upper slope. The large (>250μm) foraminifera pyrgo sp. is however, entirely restricted to the deeper regions (>1000m) of the slope (Fig.II-6). Martin (1974) has identified the most common species as P. serrata Schwager and P. murrhina Bailey.

(b) Agglutinated benthonic foraminifera (Fig.II-8 and Plate II-1).

The majority of samples contain agglutinated foraminifera and in some nearshore localities (e.g. samples 3093, 3094) these animals constitute over 50% of the total sand-size material. Although the distribution of foraminifera is limited by a variety of environmental parameters, it appears that a number of species occurring off the Cape coast are to some extent related to the composition of the ambient sediment. It has been found that four groups of agglutinates occur almost exclusively in different zones on the shelf. This is possibly due to the fact that agglutinated foraminifera require detrital grains with which to construct a shell. Numerous specimens from each group were sent to Mr. I. McMillan of SOEKOR for identification. McMillan reports that most of the foraminifera he examined are not present on the Agulhas Bank and suggests that the faunas occurring on the Bank appear to be distinguishable from both the "wholly Atlantic" and the "purely Indian" varieties to the west and east respectively. The distribution (Fig.II-8) of each group and its relationship to the bottom sediment is discussed below.

Cyclammina sp., Discammina sp. and Haplophragmoides sp:

These genera are sometimes difficult to identify as the outer chamber is invariably missing or severely damaged, and because they all appear to inhabit muddy sediment preferentially, they are grouped together.

Specimens of this group occur in the largest numbers and are most common in the nearshore faecal pellet muds in water depths of less than 200 metres. Discammina sp. is the most common variety and this is included in Martin's (1974) shallow water zone 1 group, generally <50 metres. However, this group is absent from the nearshore quartzitic sediment south of the Olifants River and from the foraminiferal and glauconitic sands on the mid shelf. Isolated occurrences are found on the upper slope west of Saldanha Bay, but in minor quantities.

The following species have been identified by McMillan:

Cyclammina cf. cancellata Brady

Discammina cf. compressa Goës

Haplophragmoides cf. crassimargo Norman

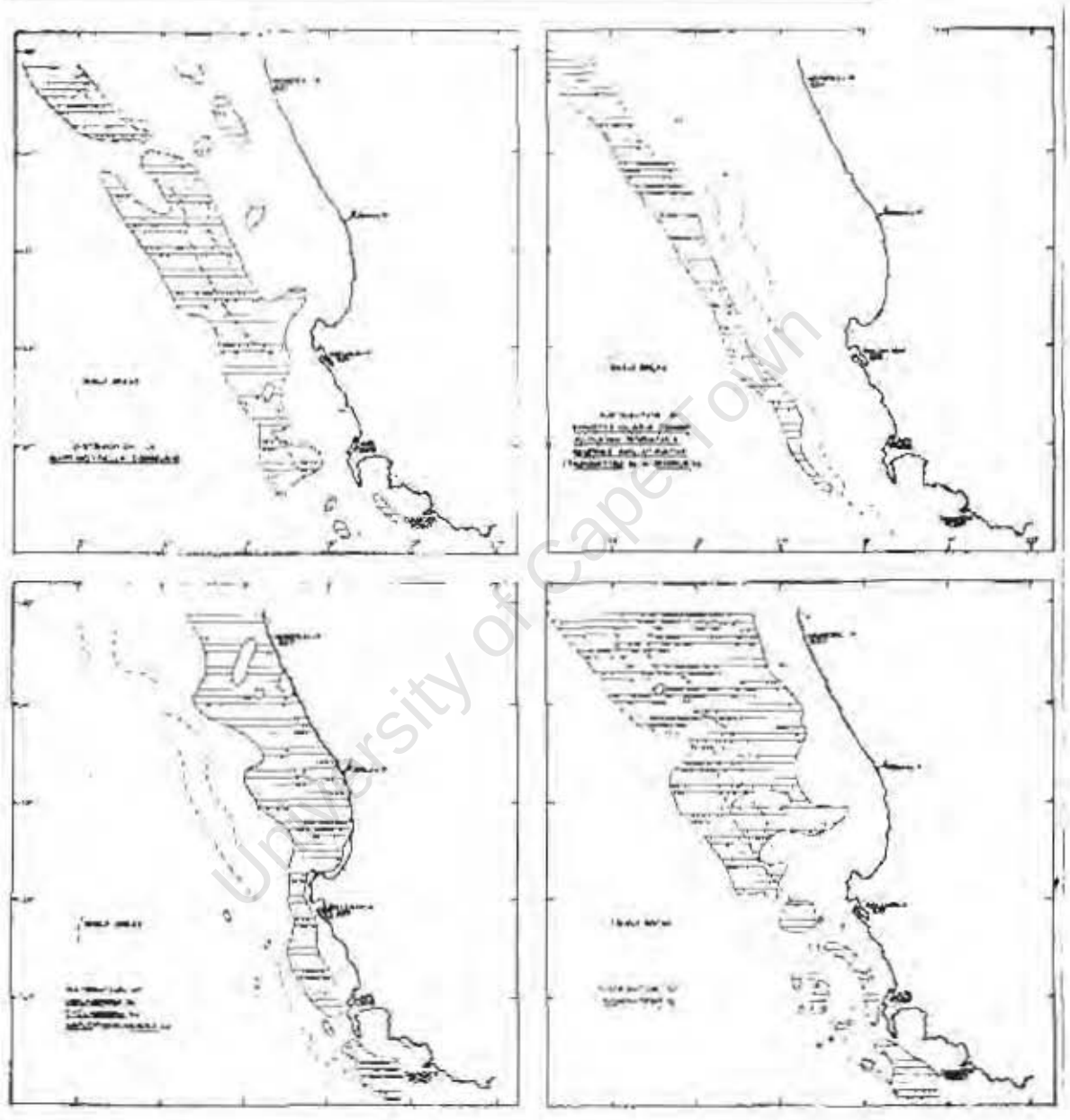


Figure II-8

Martinottiella sp. and Sigmoilopsis sp:

The distribution of these genera overlaps slightly and they occur mainly in the foraminiferal sands on the mid shelf. They are constructed with $3\frac{1}{2}\phi$ angular quartz which is a subordinate component of these sediments and do not occur where this material is absent. The distribution of Sigmoilopsis sp. extends from the inner shelf to the upper slope, whereas Martinottiella sp. is more abundant seawards of the shelf break. Martin (1974) considers the latter species to be a deep water variety and characteristic of her Zone 5 (900 metres or deeper).

McMillan has identified the following species in this group:

Martinottiella communis d'Orbigny

Sigmoilopsis schlumbergeri Silvestri

Siphotextularia sp., Vulvulina sp., Reophax sp., Gaudryina sp. or Migros sp:

This group of aggultinated foraminfera appears to be restricted to the slope environment and to sediments containing almost exclusively calcareous planktonic foraminifera and micrite. Siphotextularia sp., Vulvulina sp. and Gaudryina sp. are constructed from calcareous debris but Reophax sp. can selectively use foraminiferal tests.

Species identified by McMillan from this group include:

Siphotextularia concava Karrer

Vulvulina pennatula Batsch

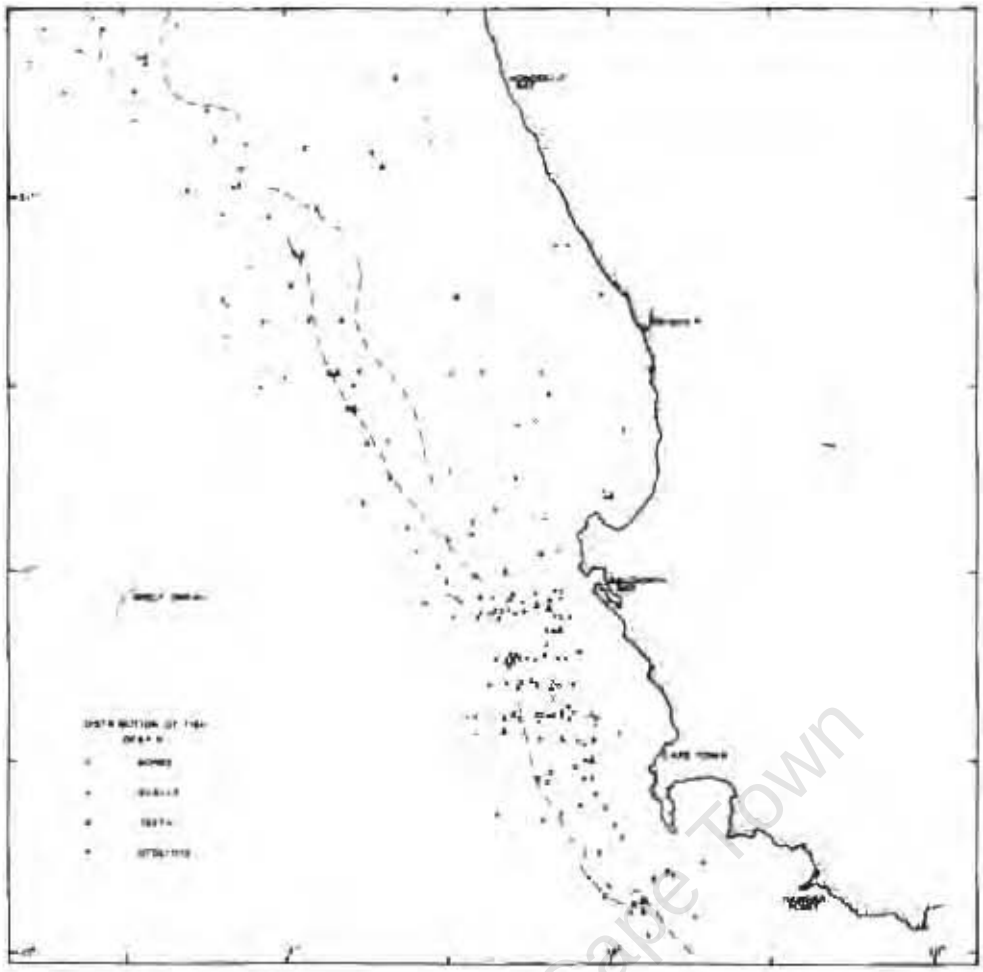
Reophax agglutinatus Cushman

(c) Diatoms and fish debris.

The distribution of diatoms and fish remains in the bottom sediment may be important in locating regions of intensified upwelling and increased fish productivity.

Diatoms are restricted to the nearshore bottom sediments north of the Berg River and west of Saldanha Bay and are most abundant in the faecal pellets muds in St. Helena Bay (Fig.II-9). In this region upwelling is generated by the prevailing off-shore summer winds(Shannon, 1966 and De Decker, 1970) and the increased nutrient content of the water (Clowes, 1954) results in enhanced biological activity and anaerobic bottom sediments (De Decker, 1970).

The diatom content is markedly lower than that occurring in a similar environment off South West Africa (pers.comm., I. Kruger, Division of Sea Fisheries, S.W.S.). This is because upwelling is less intense and more spasmodic off the western Cape (Visser, 1969) and the relatively higher oxygen content of the faster moving waters in the south (Visser, 1969) favours more rapid oxidation and dispersal of the fine organic matter. Also, the diatom species which inhabit the Cape waters are smaller and softer and therefore more susceptible to oxidation and fragmentation than are the more robust phyto-



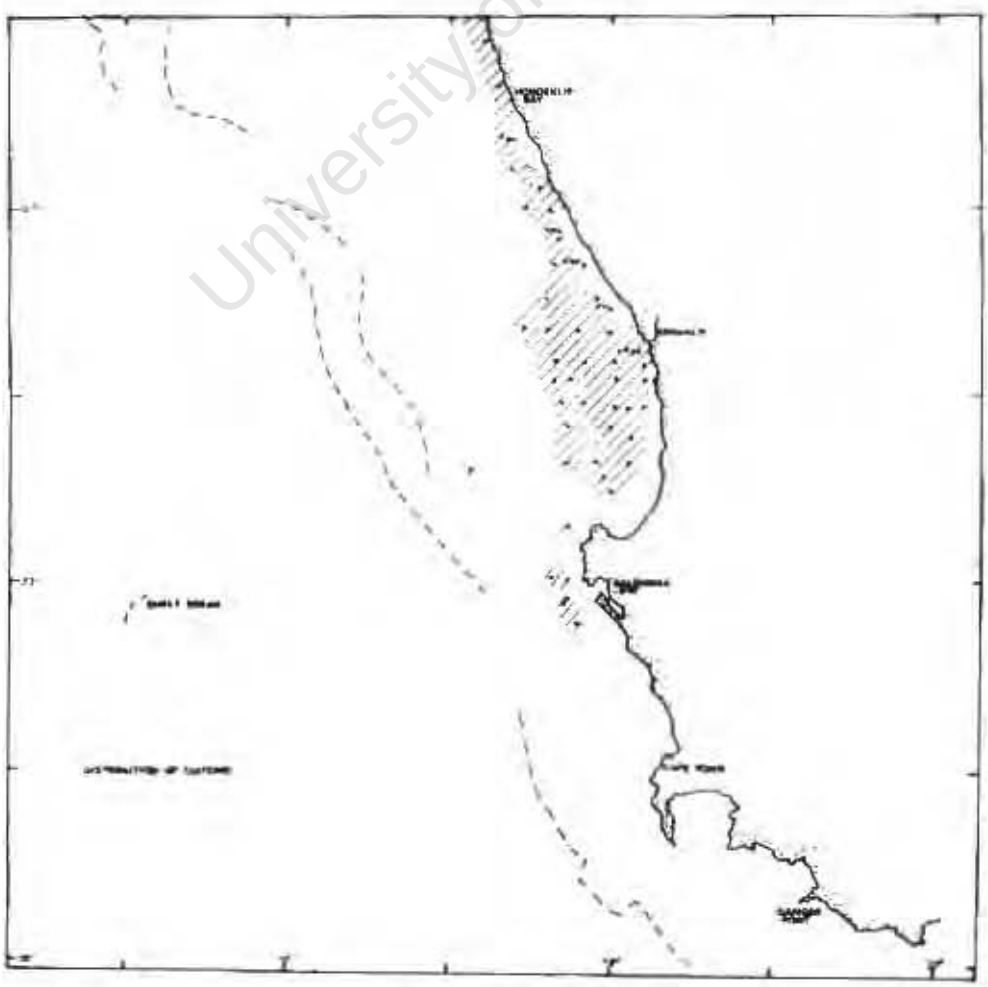


Figure II-9

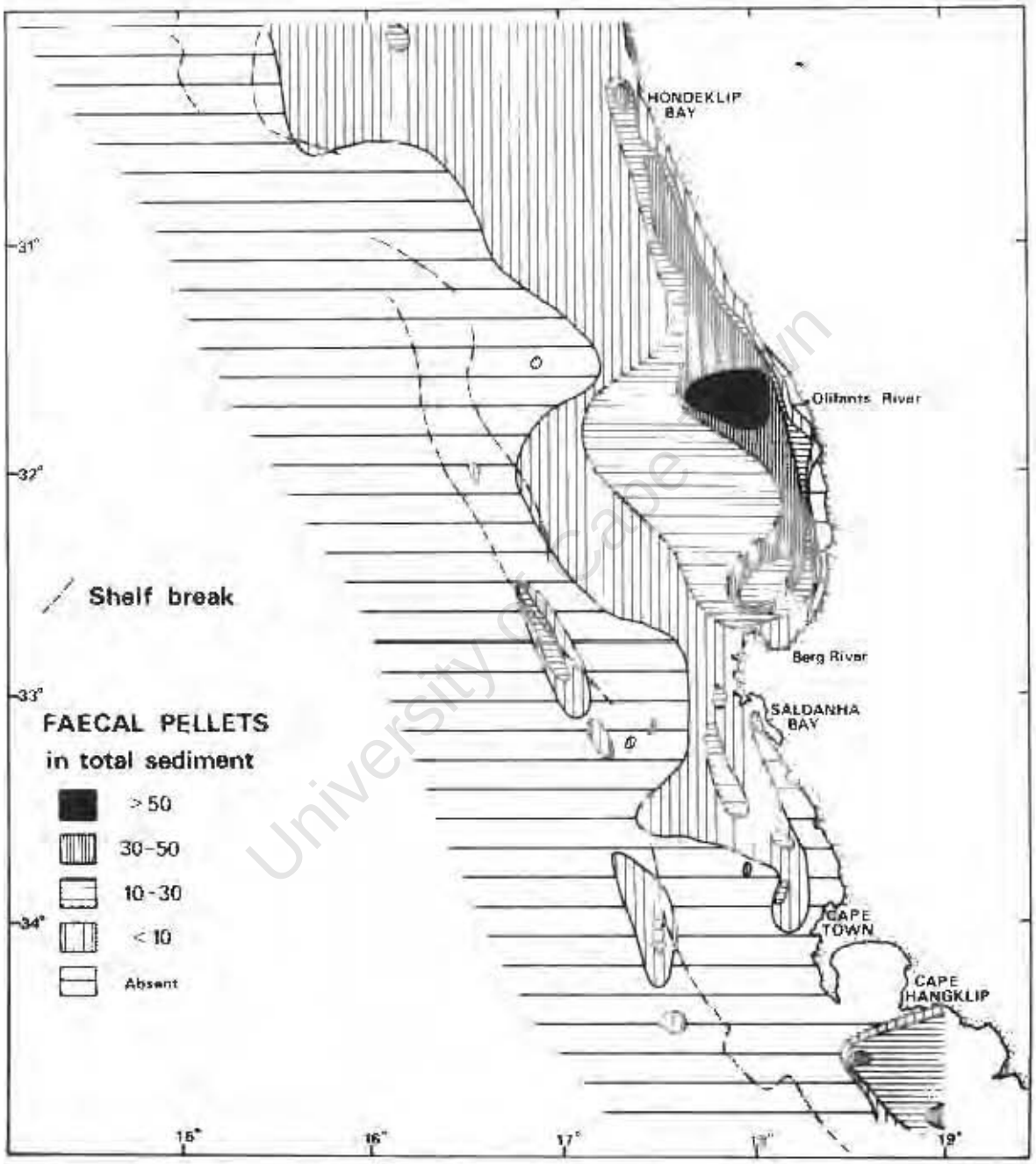


Figure II-10

plankton occurring off South West Africa (I. Kruger, pers.comm.).

Fish remains are most frequently found in the bottom sediment on the mid and the outer shelves between Cape Point and Saldanha Bay and although similar debris also occurs in the vicinity of the shelf break to the north, it is noticeably rare on the shelf in that region (Fig.II-9). Otoliths, teeth and bones are the most common type of fragment, and scales, which are not as robust, occur less frequently.

Areas rich in fish remains coincide with trawling grounds (Birch and Rogers, 1973) and also with moderately enriched organic carbon near the shelf break, but a similar association is absent in the organic-rich nearshore sediments which appear to be depleted in fish debris. Rapid burial may explain the paucity of fish remains in the nearshore region and conversely the apparent enrichment near the shelf break may be due to low sedimentation on the outer shelf.

(d) Faecal pellets.

Faecal pellets are continuously being produced by polychaete worms, namely Lumbrineris hetropoda difficilis and Diopatra monroi (N. Christie, Dept. of Zoology, UCT, pers.comm.). Removal of these pellets from the sand-size fraction has provided an estimate of polychaete worm activity (Fig.II-10).

Polychaete worms are absent in areas of low terrigenous deposition on the outer shelf and also immediately off the Olifants River mouth where sedimentation is rapid. Faecal pellets dominate the sediments on the inner shelf between the Berg and Olifants Rivers and the mid shelf south of False Bay (Rogers, 1971). In these areas faecal pellets can constitute over 90% of the sand-size sediment. A minor deep water occurrence is located on the upper slope off Saldanha Bay. The Olifants and Berg Rivers continue to supply terrigenous detritus to the faecal pellet muds north of Saldanha Bay, but the muds south of False Bay were probably deposited during the Pleistocene (Rogers, 1971) and have since been diluted by modern calcareous sedimentation.

High faecal-pellet concentrations are associated with increased organic carbon values (Fig.II-17), but the overall mineralogy of the faecal pellets is similar to that of the ambient clay. Although minor phosphatized faecal pellets occur in the outer shelf and slope sediments, nearshore faecal pellet muds exhibit low P_2O_5 values (see P_2O_5 <63μm distribution, Fig.III-4). Minor detrital phosphorite in the faecal pellet muds west of Danger Point has resulted in elevated P_2O_5 values in this area (Summerhayes, 1973).

2.5. Authigenic fraction

2.5.1. Introduction

Glauconite and phosphorite are major components of the sediment. The average glauconite content of the samples recovered is 13%, but the richest

sediment contains 86% glauconite, which constitutes over 95% of the sand fraction. The average P_2O_5 content is 1,4% and the most phosphatic sediment contains 6,8% P_2O_5.

2.5.2. Glauconite and K_2O.

The highest glauconite concentrations occur on the mid shelf at between 240 and 320 metres depth. Major deposits south of Saldanha Bay, off Lamberts Bay, and inshore west of Hondeklip Bay are well delineated from the surrounding glauconite-poor regions by sediments which contain less than 10% glauconite. Off Saldanha Bay glauconite constitutes over 80% of the total sediment over extensive areas (Fig.II-11).

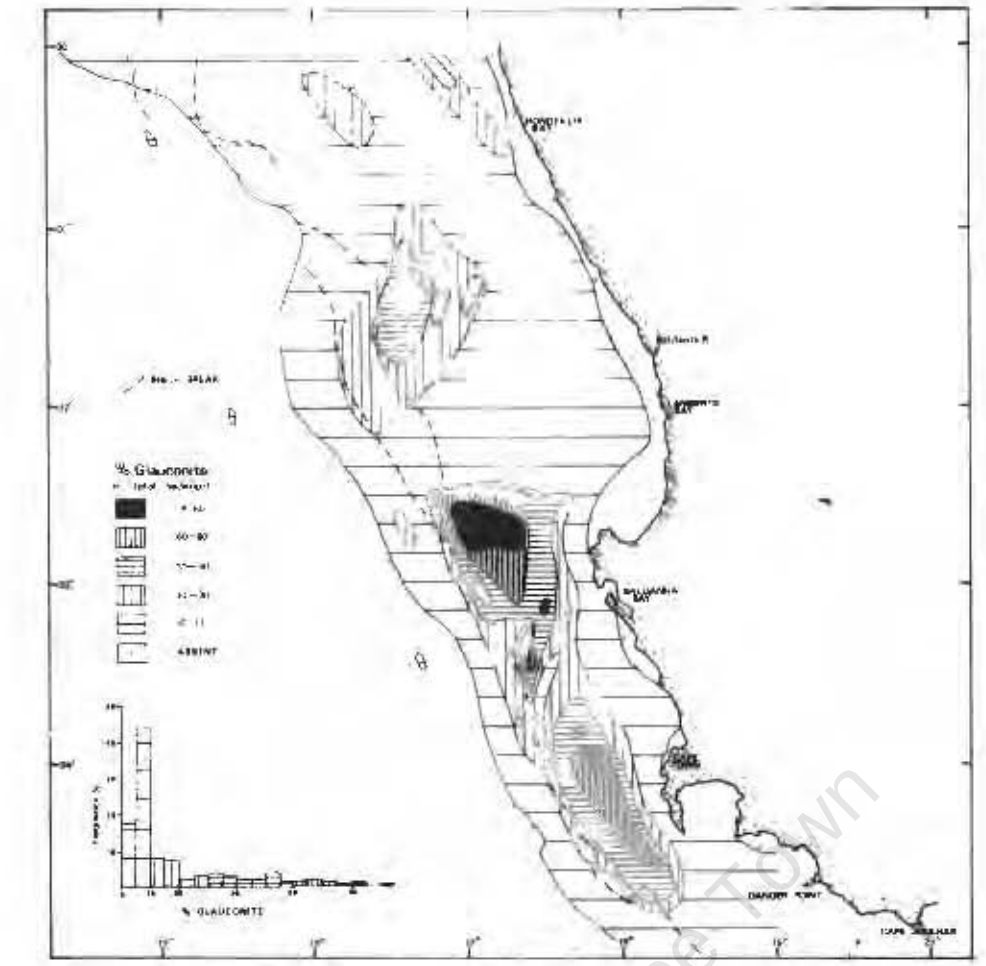
As the glauconite is relict (Birch, 1971), its true distribution is possibly better assessed if the diluting effect of Quaternary carbonate sedimentation is removed. On a carbonate-free basis, glauconite appears as a continuous mid shelf deposit throughout the area (Birch, 1973) except west of Lamberts Bay where it is diluted by terrigenous detritus. However, evidence is presented in Chapter IV which indicates that this picture is misleading and that the paucity of glauconite north of Saldanha Bay is probably due to a scarcity of this mineral in the surrounding phosphorite which is the hostrock of the glauconite.

Because the colour and morphology of the glauconite pellet reflects, to a certain extent, its chemical composition and its mode of origin, it was considered worthwhile to determine the distribution of the various types of glauconite. The abundance of five glauconite varieties was estimated using a binocular microscope and charts presented by Terry and Chilingar (1955). The same basic classification used in a morphological study of glauconite on the Agulhas Bank (Birch, 1971) was adopted in this investigation. The glauconite types distinguished are:-

(i) black to dark green, usually well-rounded glauconite with minor suturing.
(ii) light green glauconite with well-developed suturing.
(iii) yellow-green glauconite exhibiting deep sutures.
(iv) blue-green glauconite and foraminiferal casts or infillings. The shape of the blue-green variety strongly suggests that it originated as a foraminiferal infilling.

The mean size of the glauconite pellets was estimated optically to assist in determining the origin of the grain and to ascertain whether any relationship exists between glauconite abundance and pellet size.

Black or dark green glauconite is the dominant variety almost everywhere on the continental margin, except off Hondeklip Bay, in the Cape Canyon, and in the Cape Point Valley south of Cape Town. In these areas light green glauconite is the most common type (Fig.II-12). This distribution is related to the outcrop of Cretaceous or late Tertiary sediments in a similar manner to that



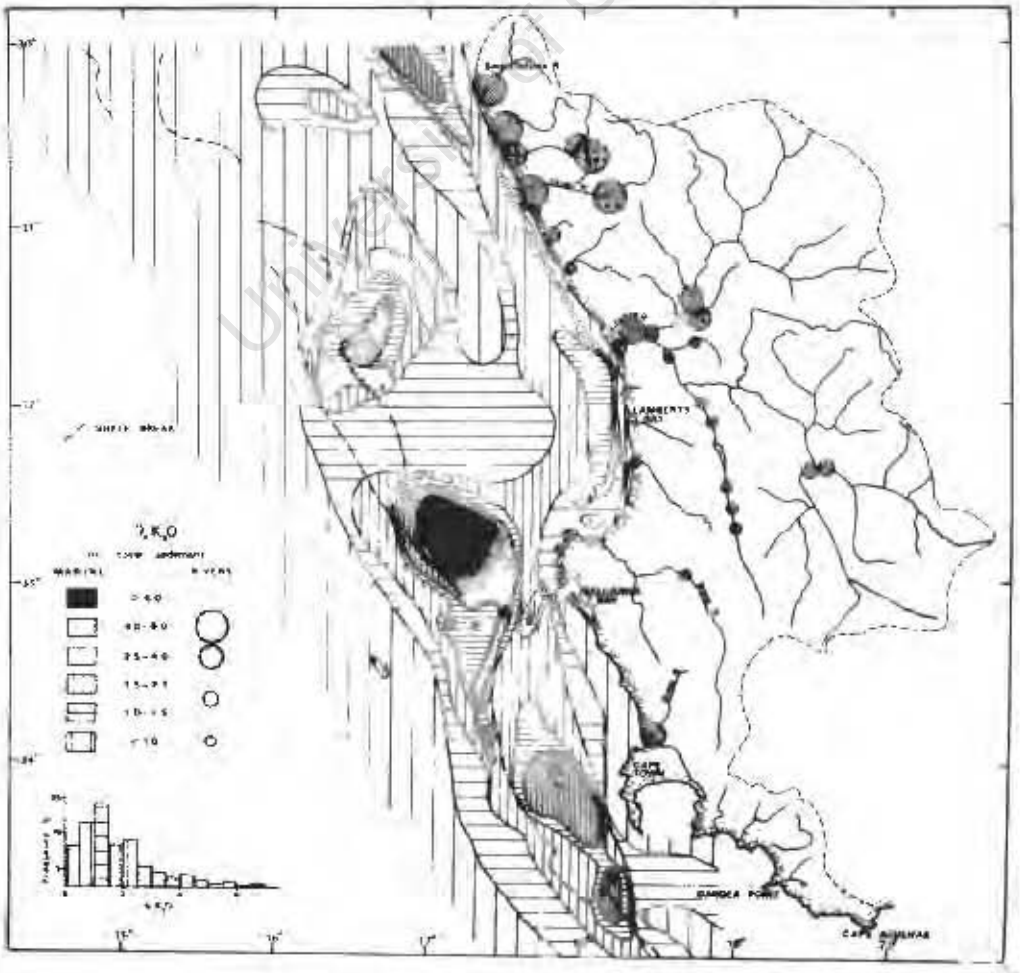
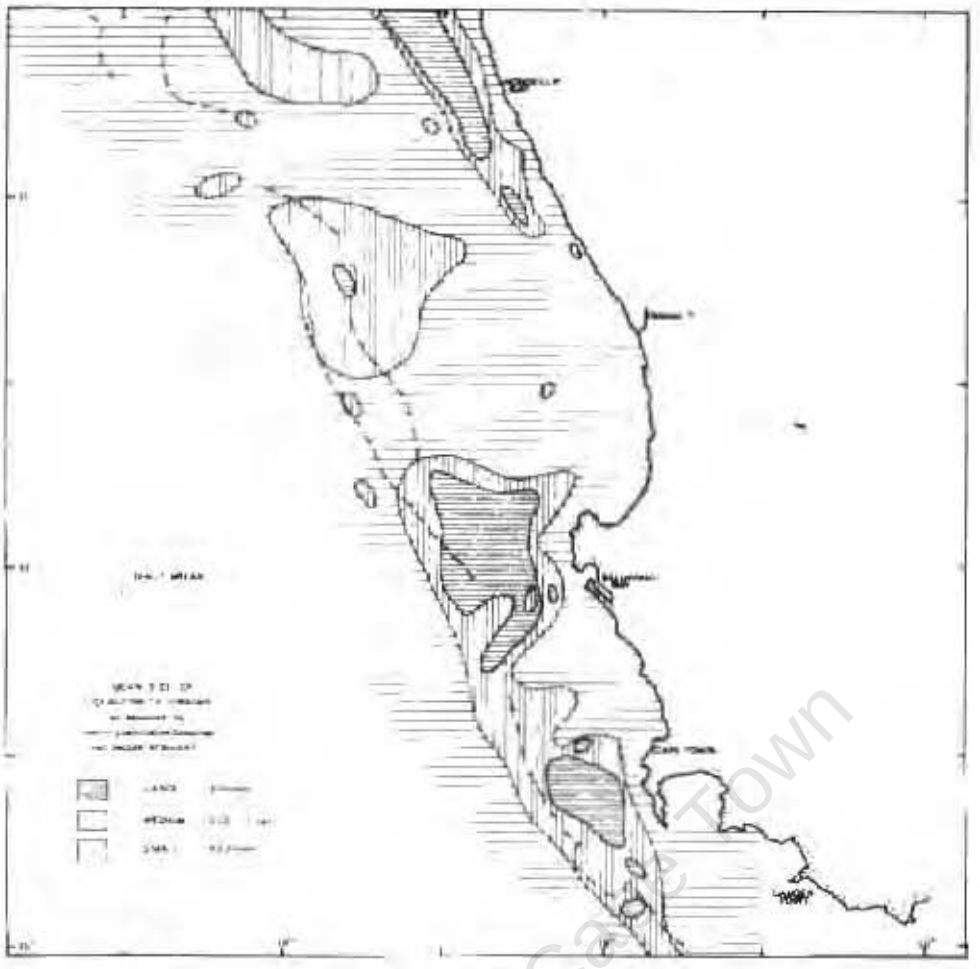
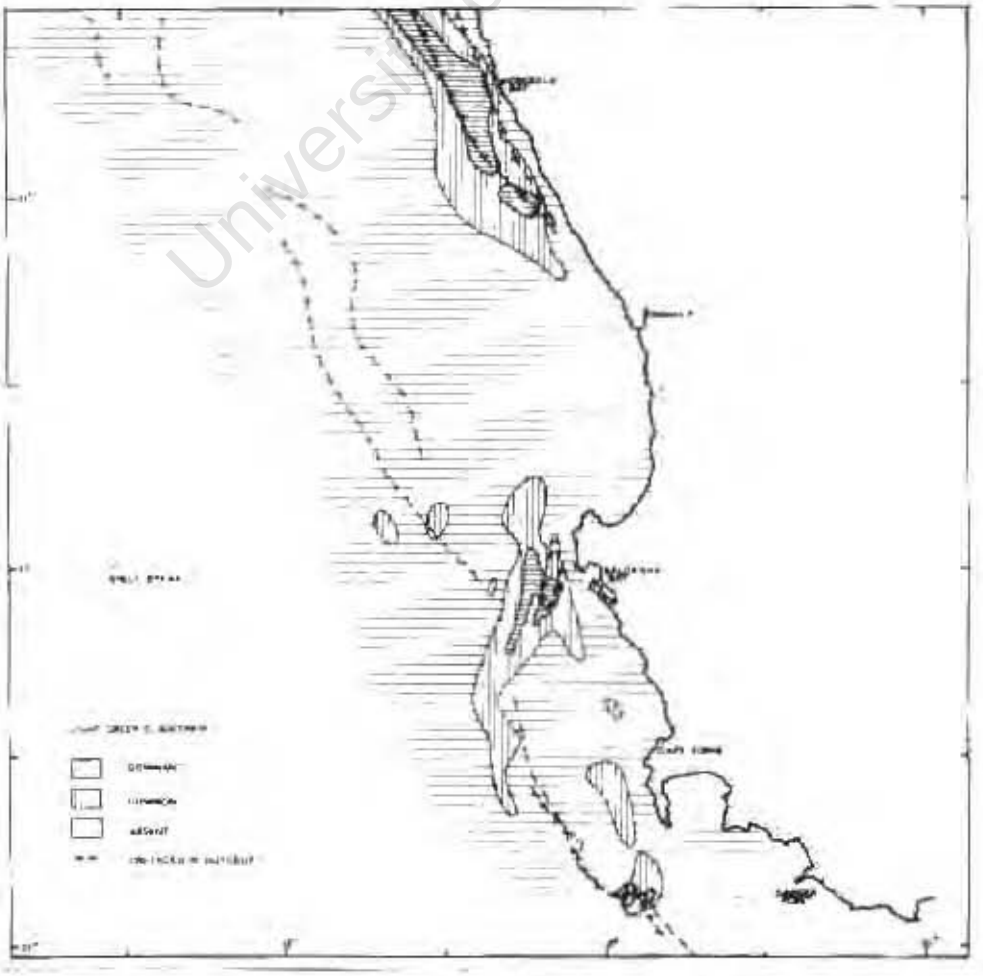
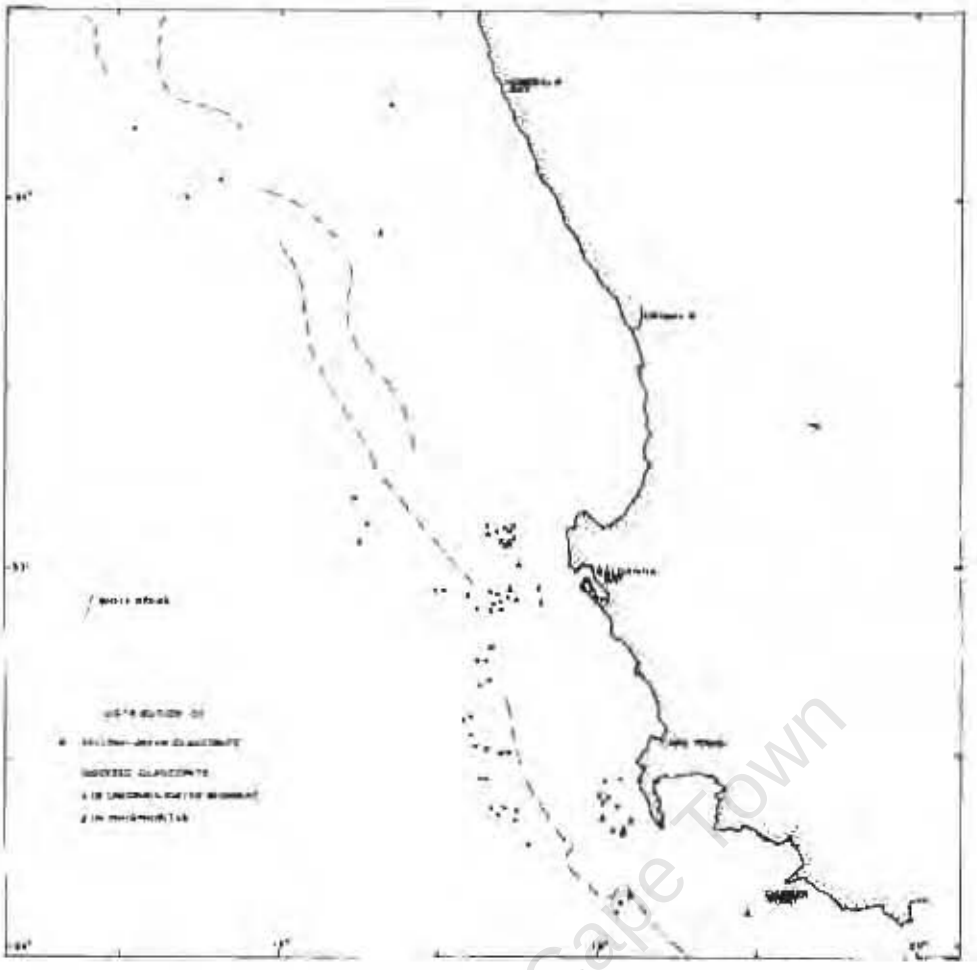
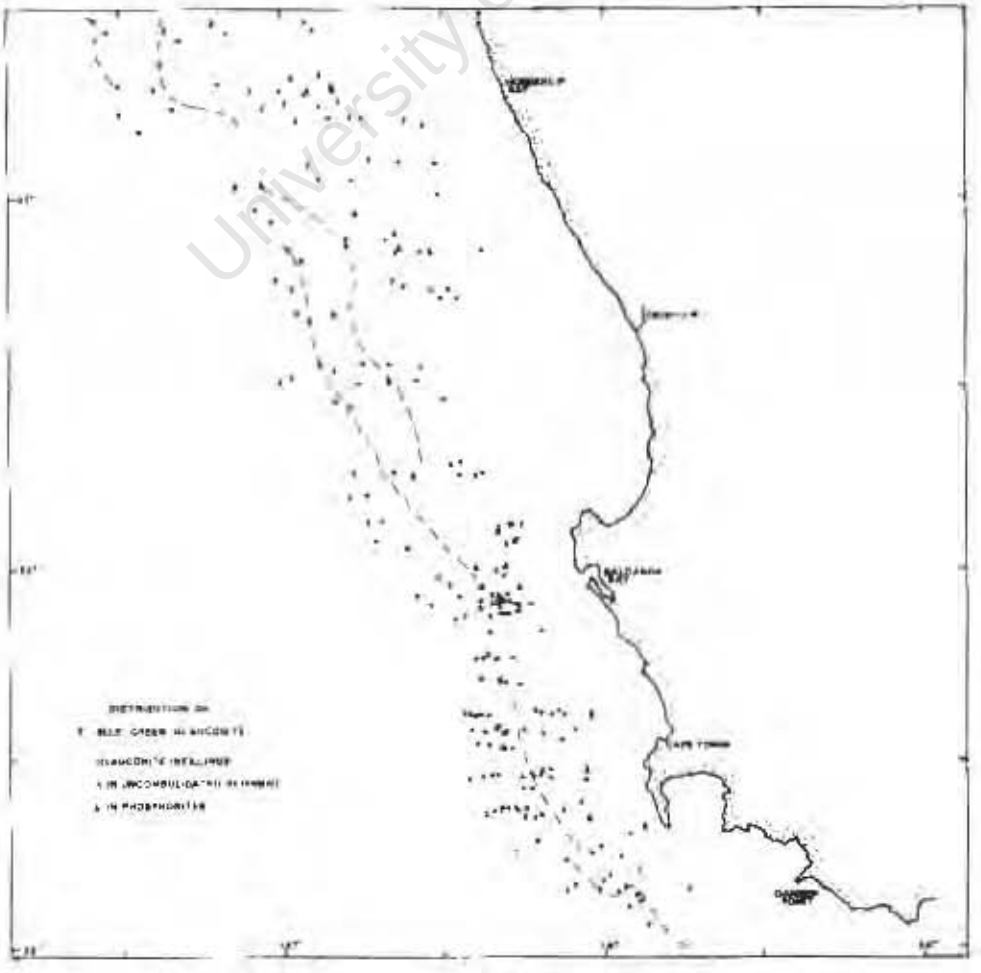


Figure II-11









seen on the Agulhas Bank. Yellow-green, highly sutured glauconite is most common in sediments from the slope, especially in the region south of Saldanha Bay (Fig.II-13). Minor occurrences are also found on the mid shelf off Saldanha Bay and Cape Town. The low potassium content (Chapter IV) and primary morphology exhibited by these glauconites (Birch, 1971) indicates that authigenesis ceased prematurely, possibly due to increased sedimentation and rapid burial which effectively screened the pellet from overlying potassium-rich sea water.

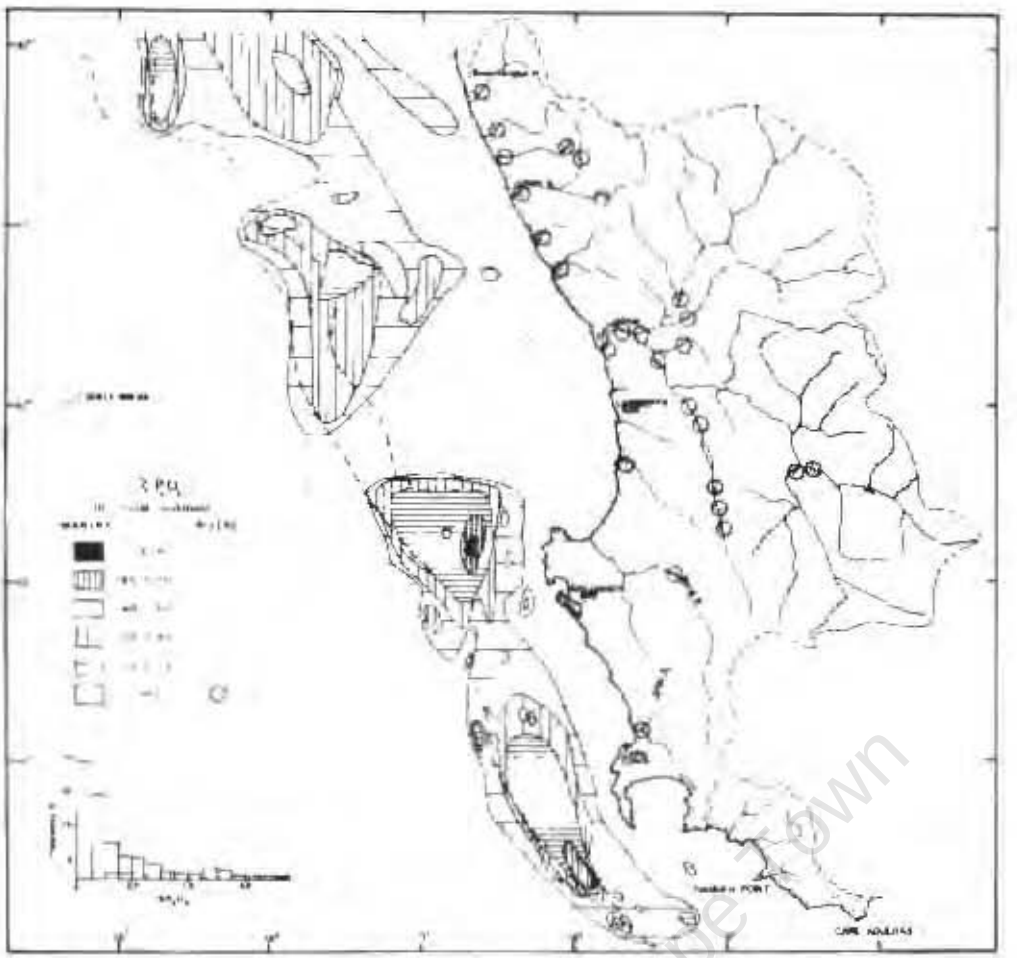
The blue-green glauconite and foraminiferal casts are most abundant in the highly fossiliferous slope sediments, but minor blue-green pellets also occur in the foraminiferal mid-shelf sands off Hondeklip Bay (Fig.II-13). These glauconite varieties are probably less common on the shelf because they could not survive vigorous erosion during the transgression/regressions cycles. This probably also applies to the less robust primary morphologies of the yellow-green pellets.

The distribution of oxidized glauconite grains in the unconsolidated sediment correlates fairly well with their occurrence in phosphorite rocks (Fig.II-13), but this relationship is not as clear for foraminiferal casts (Fig.II-13). This evidence is in accord with the view that the glauconite is derived from the underlying phosphatic sediments (Birch, 1971).

The mean size of the glauconite pellets as estimated during this binocular microscope examination correlates well with the results of the total component sieve analyses discussed earlier in this chapter. The dark green or black glauconite off Cape Town and Saldanha Bay are commonly over 0,5 mm in size (medium-sand size) and the light green pellets from the Hondeklip Bay deposit are probably more common in the coarse sand-size fraction (Fig.II-12). The pellets are largest in the most glauconitic sediment, probably because these regions provided optimum conditions for glauconitization and because the grains that were reworked and transported away from the source were disaggregated and abraded.

The foraminiferal sediment on the shelf off Hondeklip Bay is fine sand, and the glauconitic sediment off Saldanha Bay and west of Cape Town is mainly medium sand (Figs.II-3 and 4 respectively). It is unlikely, even accounting for pellet expansion during diagenesis, that the majority of the glauconite could have originated as foraminiferal casts. This is especially evident when the average coarse sand-size of the pellets from the Hondeklip Bay deposit is considered.

Glauconite was concentrated electromagnetically, but because this mineral is frequently diluted by substantial quantities of apatite (see Chapter IV) some glauconite is possibly lost to the non-magnetic fraction (ie. non-glauconite component). A better assessment of the pure mineral phase may thus be



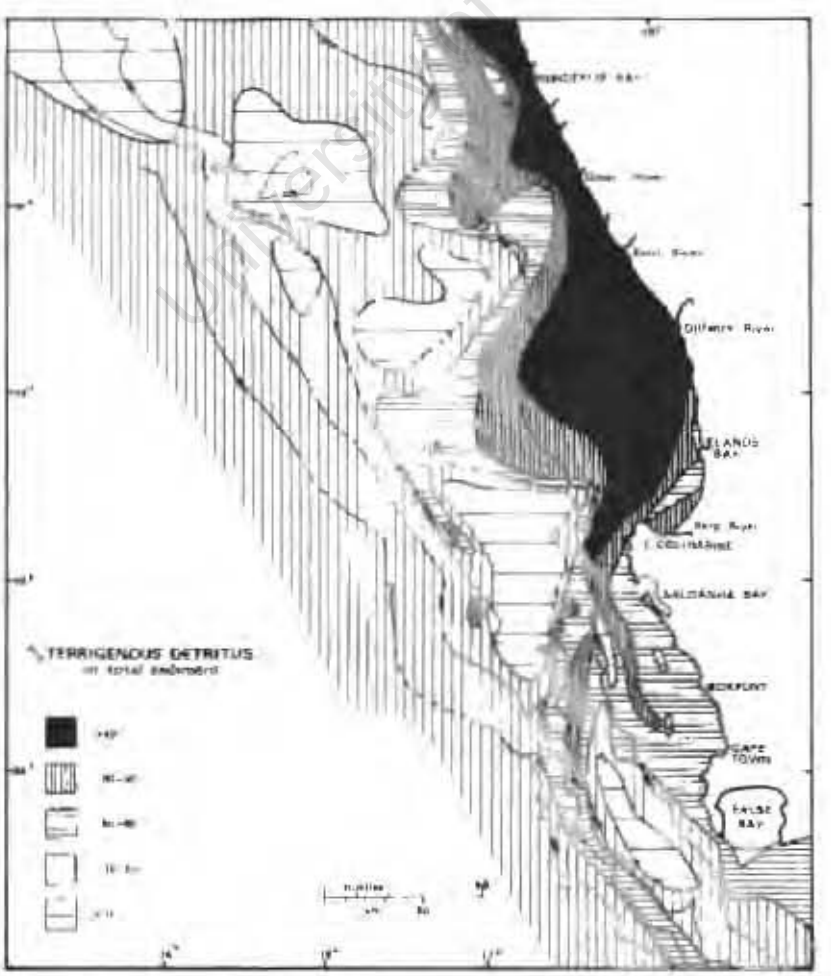


Figure II-14

obtained by determining the K_2O content of the total sediment. However, the similarity in the distribution of the two parameters (Figs.II-11) indicates that the magnetic separation is an effective analytical technique. A fairly close statistical correlation between K_2O and glauconite (Figs.II-11 and 17)(correlation coefficient 0,68) implies that glauconite is the primary K-mineral present in the sediment. Minor K-enrichment owing to considerable influx of K-rich clay minerals was noted on the inner shelf off the Olifants River.

The mean K_2O content of the samples, 1,9%, is approximately average for non-calcareous marine sediment (Turekian and Wedepohl, 1961), but the large maximum value (7,1% K_2O) reflects the abnormally high glauconite content of the sediment.

2.5.3. Phosphate (P_2O_5).

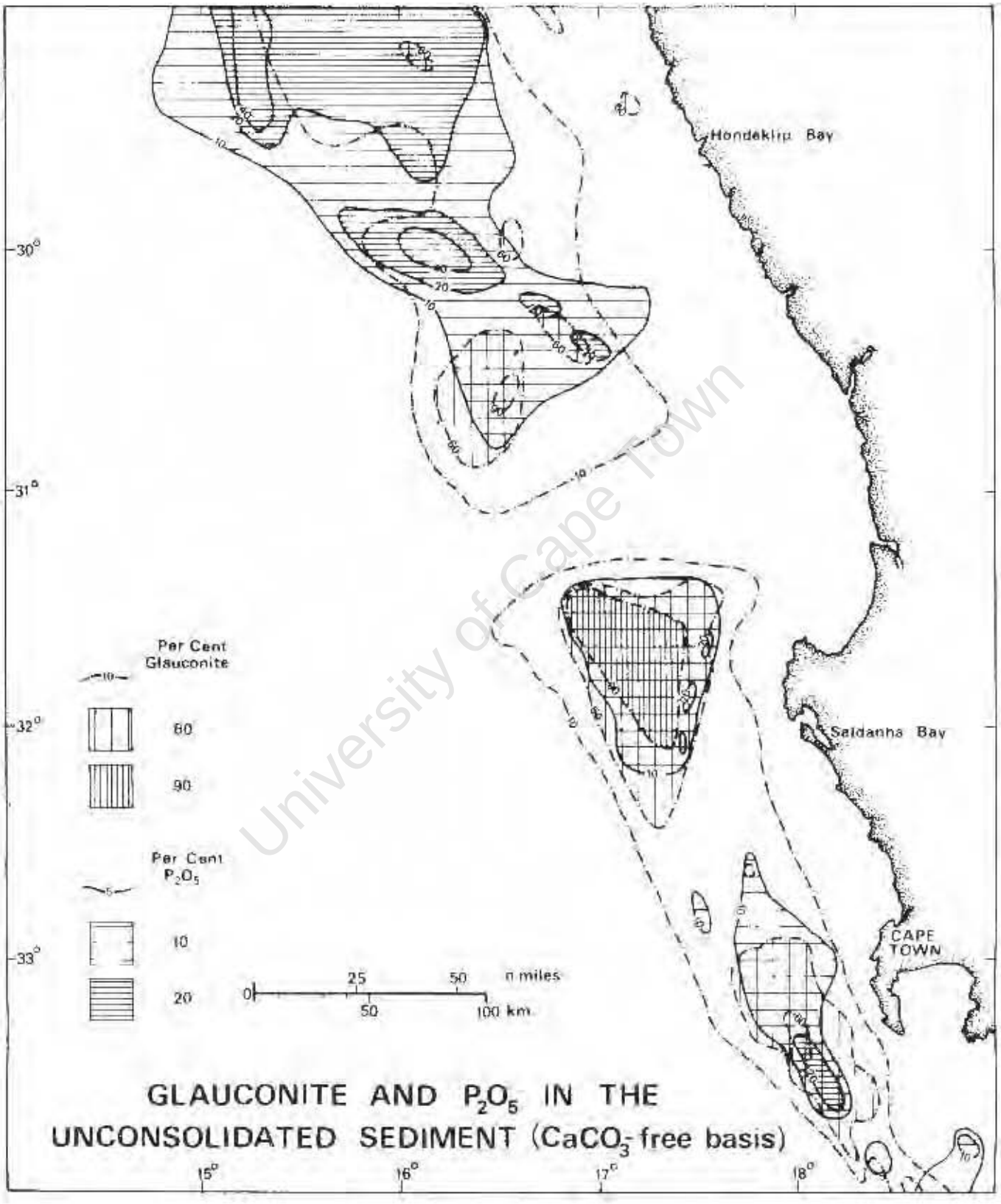
The distribution of phosphate in the total sediment follows closely that of glauconite. The main phosphate deposits occur off Cape Town, Saldanha Bay and Olifants River, and minor outer shelf phosphate-enrichment is apparent off Hondeklip Bay (Fig.II-14).

When the diluting effects of carbonate sedimentation are removed the phosphate deposits in the north are greatly enriched (up to 15% P_2O_5), but otherwise the distribution remains unchanged (Birch, 1973, Fig.VIIIA-15).

An attempt was made to determine the distribution of several phosphorite types observed in the sediment, but this was not successful. However, distinctive resinous brown pelletal phosphorite occurs on the outer shelf and south of Childs Bank upper slope (Numbers 3346 and 3576) and west of Danger Point (Numbers 295, 296 and 308). These pellets are well rounded and frequently contain an organic-rich core. Silt-size quartz is sometimes also present. These pelletal phosphorites closely resemble those from the mid and the outer shelves off South West Africa (Summerhayes et al., 1973) and are also similar to the onland deposits. Fine-sand size faecal pellets from the continental slope off Cape Town are occasionally phosphatized.

2.5.4. The regional relationship between glauconite and phosphate.

It is evident (Fig.II-15) that in some areas of the continental shelf glauconite and phosphate minerals are intimately related, whereas in other regions they occur separately (Summerhayes, 1973). Some of the major authigenic belts of the west coast contain both abundant glauconite and phosphate, but off Hondeklip Bay and on the Agulhas Bank these minerals occur in zones which are slightly offset. P_2O_5 values generally increase with glauconite concentration (Fig.II-17) and a statistical correlation of all samples (correlation coefficient P_2O_5 vs glauconite for 503 samples is 0,68) would be significantly closer if the sediment to the north of Olifants River was excluded.



GLAUCONITE AND P_2O_5 IN THE UNCONSOLIDATED SEDIMENT ($CaCO_3$-free basis)

Summerhayes (1973) and Summerhayes et al. (1973) have related phosphate in the sediment to the underlying Tertiary strata. Glauconite, on the other hand, is present in both Cretaceous and Tertiary sediments (Birch, 1971), but it is not always associated with one particular stratigraphic horizon. For example, the sediments comprising the Pliocene Childs Bank Formation (Dingle, 1973(a)) are highly glauconitic off the Cape Peninsula and west of Saldanha Bay, but are glauconite-poor on Childs Bank.

Studies of individual glauconite types (Birch, 1971 and Summerhayes, 1973) indicate that black varieties, derived predominantly from Tertiary phosphorites are commonly phosphatic, whereas light green and yellow-green glauconite, generally weathered from older, more argillaceous formations is less phosphatic. The mineralogy and geochemistry of these two mineral phases is discussed in more detail in Chapter IV.

2.6. The terrigenous fraction

2.6.1. Introduction.

The terrigenous component of the sediment was calculated by subtracting the combined weight percentages of glauconite, biogenic carbonate, organic matter and carbonate apatite from 100%. This value will of course be subject to the combined experimental errors incurred in obtaining the four determinations, but this is considered acceptable for the purposes of this study.

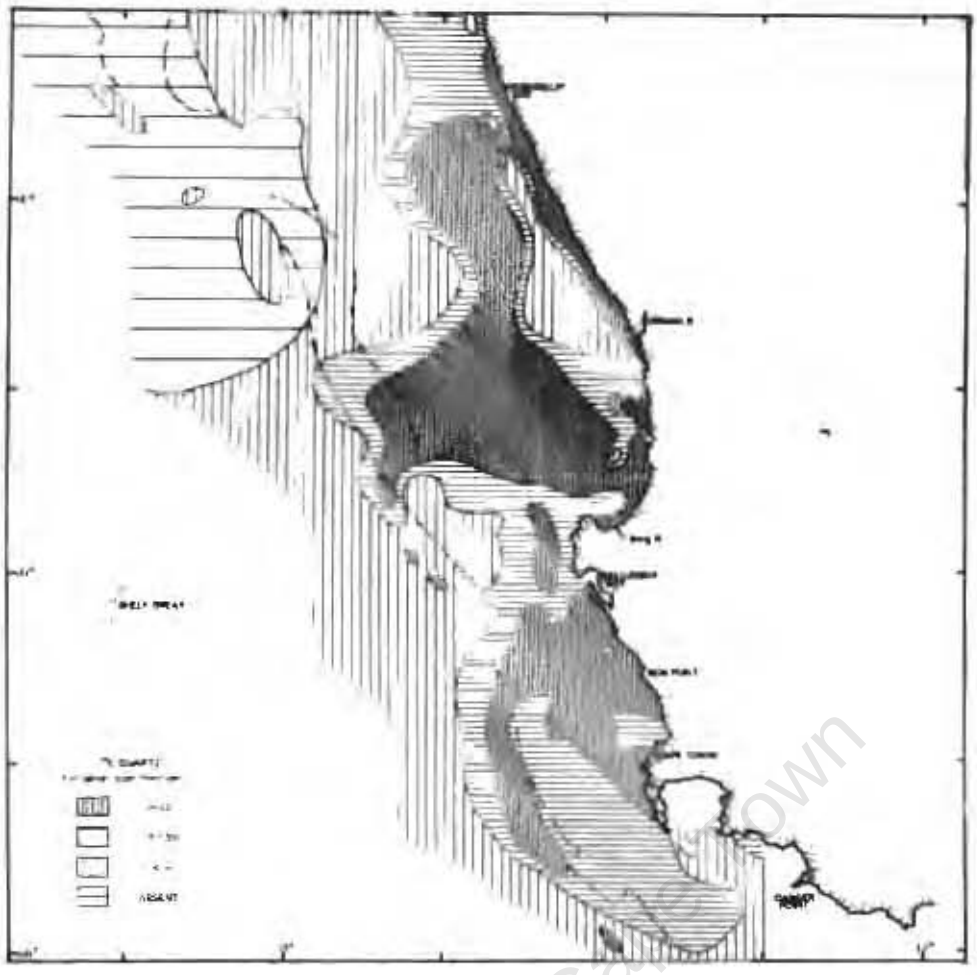
Terrigenous-rich sediment mantles the inner shelf throughout the region as well as the upper slope west of Cape Town, but off the Olifants River it covers the entire width of the shelf (Fig.II-14).

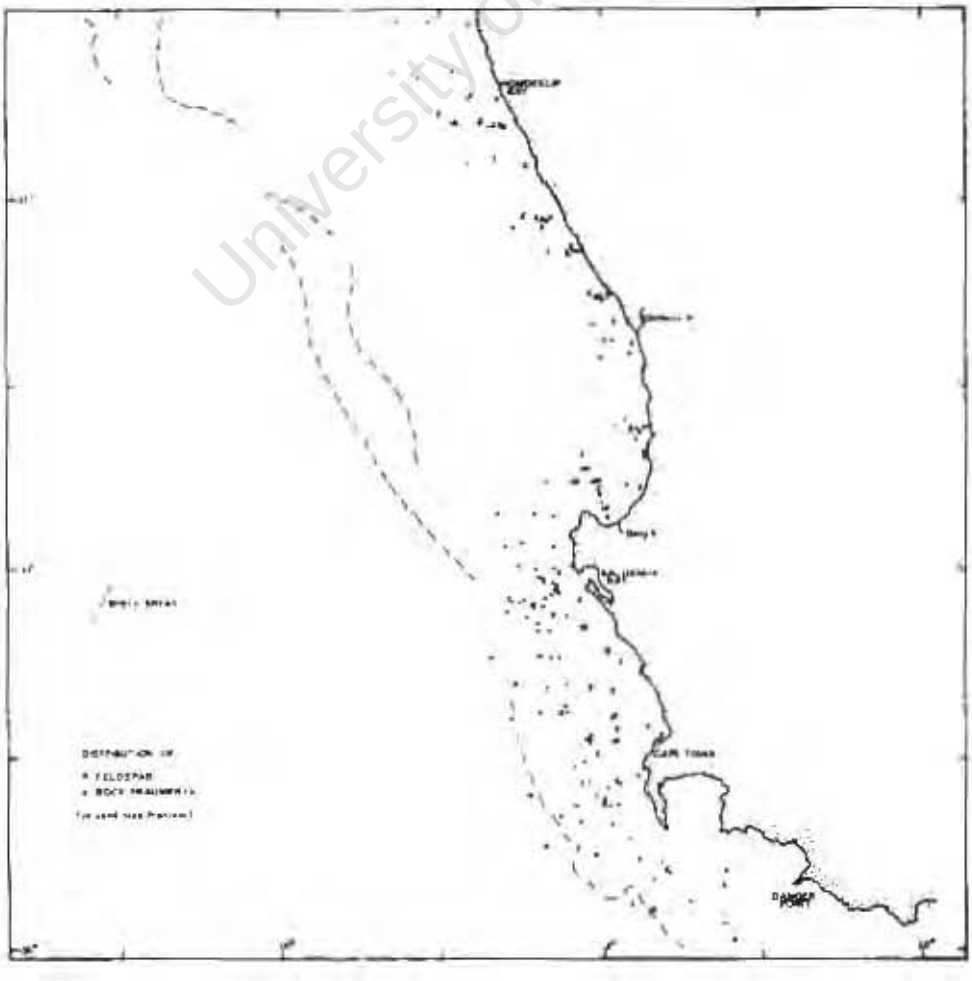
The abundance of the major terrigenous components, quartz, rock fragments and feldspar, has been estimated by carrying out a binocular microscope examination of the sand-size fraction in a similar manner to that described for the biogenic and authigenic sediment. The nature and distribution of these terrigenous components are briefly described below.

2.6.2. The quartz component.

Highly quartzitic sediment (>50% quartz) mantles much of the mid shelf north of Saldanha Bay, but quartz abundances are noticeably lower in the glauconite-rich sands off Saldanha Bay and Cape Town and in the foraminiferal sediment west of Hondeklip Bay. Faecal pellets were not removed in this investigation and therefore quartz values are low (<5%) in the faecal pellet muds directly off the coast north of the Berg River. However, if the pellets were regarded as part of the mud fraction, quartz would undoubtedly constitute a major portion of this sediment as well.

A comparison of quartz abundance with the total component size data presented in Figure II-3 clearly indicates that the quartzitic sands off the Olifants River and Bokpunt are almost entirely very fine-sand size (Fig.II-20).





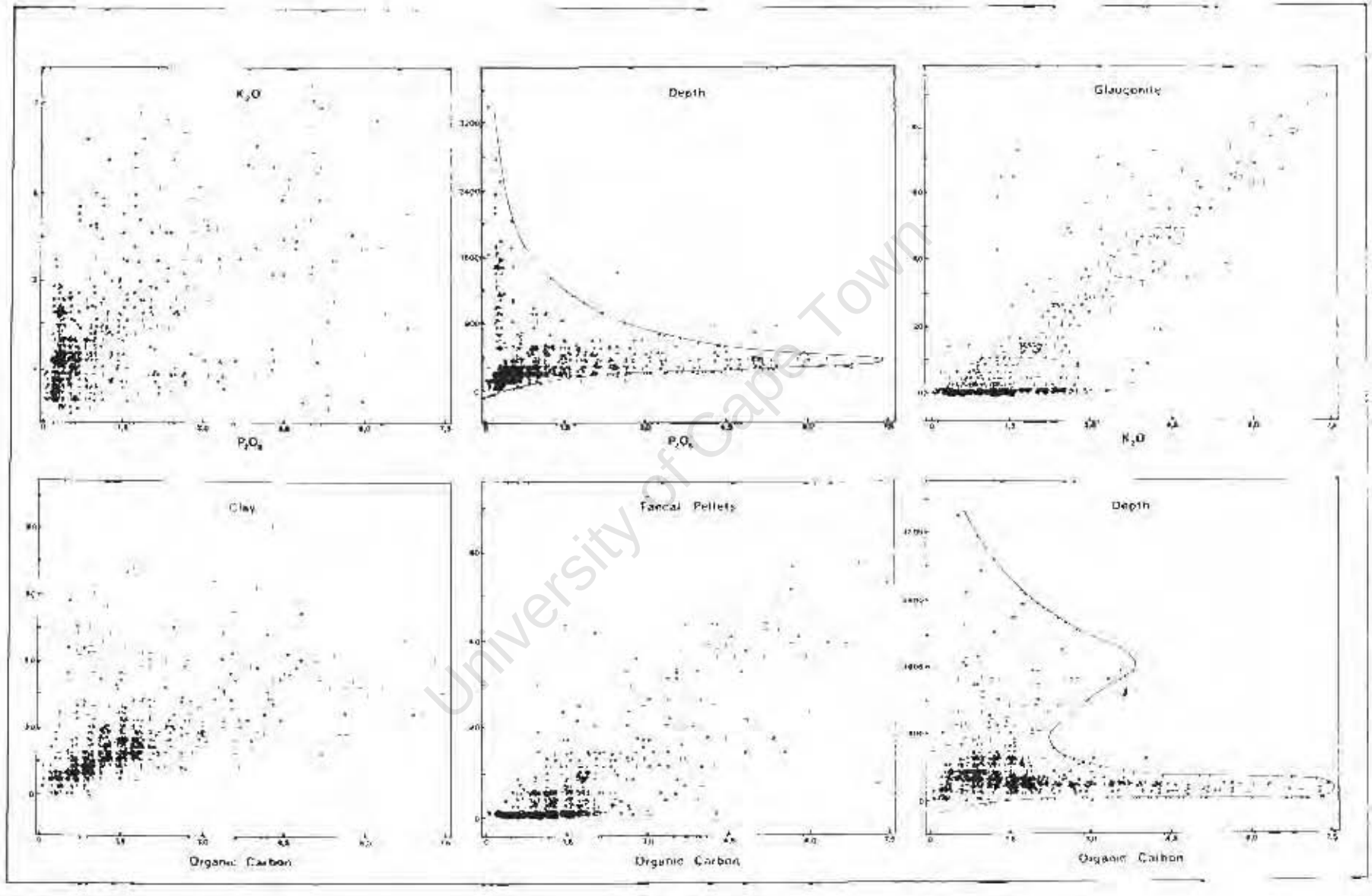


Figure II-17

2.6.3. Feldspar and rock fragments.

Rock fragments occur irregularly on the inner shelf south of Saldanha Bay, but off the Berg River and between the Olifants River and Hondeklip Bay rock fragments are common (Fig.II-16). South of the Olifants River rock fragments are composed mainly of quartzites and shales with minor limestones, whereas to the north fragments of schist and gneiss are more common. This distribution closely reflects the composition of the local onland geology (Fig.III-1).

Feldspar is more widespread than rock fragments in the sediment and its occurrence does not appear to be related to present-day influx of terrigenous sediment. Instead, large feldspar grains exhibiting a well-defined cleavage are common in the glauconitic sediments off Saldanha Bay and Cape Town (Fig.II-16). These minerals, like glauconite, have probably been eroded from the shelf substrate. Feldspar is also present off the Berg River and in the quartzitic sediments on the slope south of Saldanha Bay.

2.7. Generalized sedimentary facies

Mineralogical and textural data have been combined and simplified in an attempt to group the sediments into regions of similar composition and size characteristics (Fig.II-18).

A broad swathe of terrigenous sediment extending across the shelf west of Elands Bay separates two regions of markedly different sedimentary character. In the north foraminiferal sands and muddy sands mantle the slope and much of the shelf, and only minor glauconite is present west of the Olifants River. Towards the inner shelf these sediments become increasingly muddy and quartzitic until immediately seawards of the rocky coastal platform, faecal pellet mud predominates. Depressions on the platform are filled or partially filled with shelly quartzitic sands and gravelly sands (O'Shea, 1971).

The sediment pattern south of Elands Bay is complicated by exposure of Tertiary and Cretaceous sediment, by the Cape Canyon and by the presence of a rich residual authigenic component. Highly glauconitic sand on the mid shelf is generally diluted by quartzitic sediment shorewards, and foraminiferal sand and muddy sands mantle the slope. West of Saldanha Bay and Cape Town muddy quartzitic sand separates the glauconitic sediment from the foraminiferal muds on the slope.

The basic sedimentary pattern therefore comprises three regimes: 1) nearshore muddy and sandy terrigenous Quaternary sediments; 2) biogenic Holocene sediment composed of foraminifera and coccolithophorids (Rogers, 1973) on the slope; and 3) an intermediate region of mixed Tertiary sediment composed of mainly relict or residual authigenic components.

The outer shelf sediments off the Olifants River are too thin (<1 metre) to be resolved by boomer seismic apparatus and even the quartzitic muddy sands on the inner shelf in this area are less than one metre thick (Du Plessis, pers.comm.). The faecal pellet muds immediately seaward of the coastal platform are, however, generally about 15 metres thick. Coring has confirmed the thickness of the inner shelf sediments and has also disclosed that they are underlain by shelly sands and gravels containing a rich quartz component (approximately 50%).

2.8. Sediment colour

2.8.1. Introduction.

The colour of the sediment is described after the composition has been discussed to enable the two parameters to be more easily compared.

The colour of sediment can be indicative of composition of the material if it is crushed to eliminate inhomogeneities. The crushed samples used for chemical analyses were separated into four groups which correspond with the main sedimentary types. Terrigenous muddy sediments are olive-gray; foraminiferal sands and muddy sands are yellow-gray; glauconitic sediment is green; and a small group of shelly quartzitic sand from the coastal platform is yellowish- and pinkish-gray.

Colour, in addition to indicating the general components of the sediment, can also reflect, in broad terms, the concentration in which they occur. For example, an increase in the glauconite content of sediment is accompanied by a general increase in chroma, and a decrease in value (5GY7/2->5GY6/2->10GY5/2->5GY5/2, Munsell colour code values). It was thus possible to establish series of standard samples within each group which were related to mineralogy. Crushed sediment was compared directly with reference samples.

2.8.2. Sediment colour and its relationship to composition.

The sediment composition map (Fig.II-18) and the sediment colour chart (Fig.II-19) show similar trends.

An increase in chroma and a decrease in value within the olive-gray hue group (5Y5/4->5Y5/2->5Y4/4) corresponds to an increase in the abundance of faecal pellets, but a decrease in chroma and an increase in value in the yellow-gray hue group (5Y6/4->5Y8/2) is related to an increase in value in the carbonate content of the sediment. Similarly, an increase in glauconite concentration is accompanied by a general increase in chroma and a decrease in value within the green hue group (5GY7/2->10GY5/2->5GY5/2). Dilution of glauconite by faecal pellet mud results in a grayish-olive hue (10Y5/2; 10Y4/2 and 5GY4/2), whereas a carbonate diluent produces a pale olive hue with a higher value (10Y7/2 and 10Y6/2).

Two samples from within the faecal pellet mud off the Olifants River

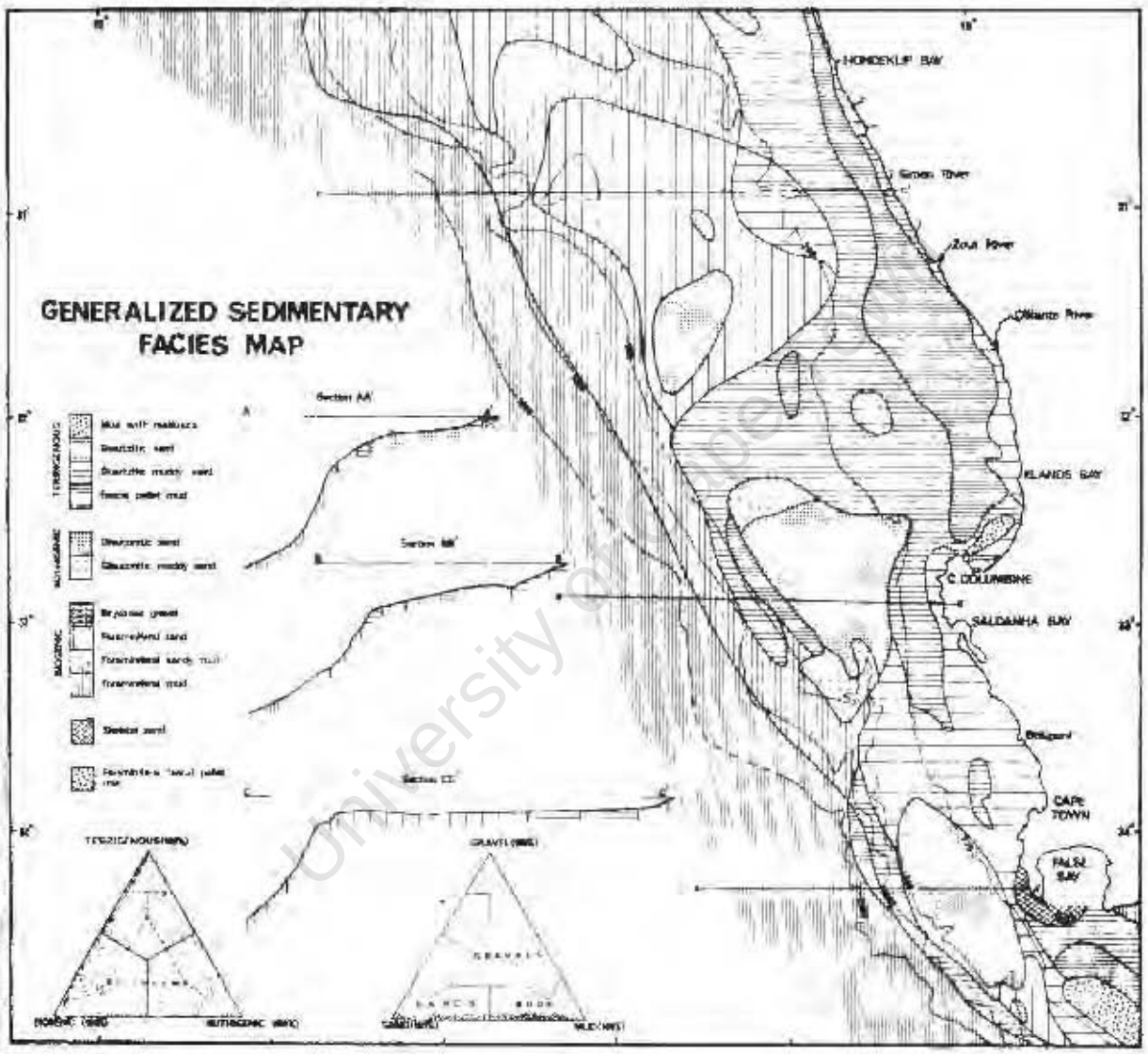

GENERALIZED SEDIMENTARY FACIES MAP
HONDEKLIP BAY
Groen River
Zout River
Olifants River
KLAWER BAY
C. DOLUMBINE
SALDANHA BAY
Bokkeveld
CAPE TOWN
FALSE BAY
Section AA'
Section BB'
Section CC'
TERRIGENOUS
MIXED
BIOGENIC
Mud with molluscs
Bioturbitic sand
Glauconitic sand
Glauconitic muddy sand
Bryozoan gravel
Foraminiferal sand
Foraminiferal mud
Skeletal sand
TERRIGENOUS MUD
NORMAL SAND
AUTHIGENIC SAND
GRAVELLY
SANDS
MUDS
CARBONATE
MUD

Figure II-18

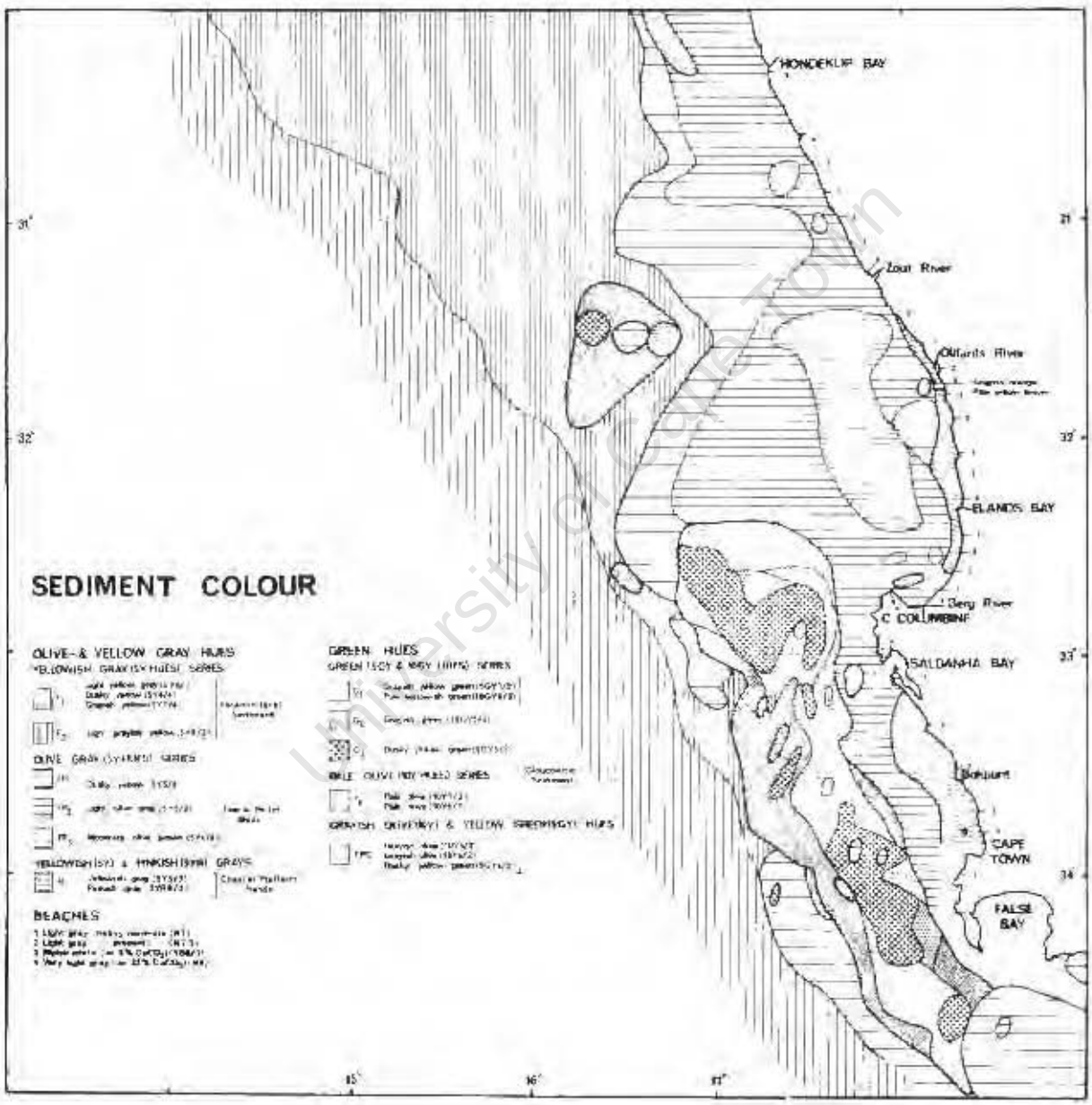


Figure II-19

contain no faecal pellets and are rich in plant fragments. These samples are anomalously grayish orange (10YR7/4) and pale yellow brown (10YR 7/2).

An increase in the carbonate content of beach sediment is accompanied by a decrease in chroma and a shift in hue (5B8/1->N8) and minor quantities of heavy minerals are detectable by a slight decrease in value with regard to other beaches (N7 and N7,5).

2.9. Sedimentary history

Sediments on the continental margin comprise a mixed population, the components of which have originated from three dominant processes; fluvial influx, authigenesis, and deposition of biogenic debris. Products of these mechanisms represent various ages and many depositional environments, and can be grouped into modern, relict or residual components. Residual sediment is a product of *in situ* weathering of bedrock; relict material is a remnant of an earlier, different environment. Swift et al. (1971) suggested the term "palimpsest" for a relict sediment that is mixed with a modern component, normally silts and clays.

2.9.1. Palimpsest sediment.

Since all the relict and residual sediments on the mid and the outer shelves have at least a minor modern calcareous or terrigenous component, they should strictly be classified palimpsest.

The coarse grain size of off-shore sands on the Californian shelf was the major criterion used by Emery (1952) to define relict sediment, and phosphorite and glauconite have been used as indicators of residual material (Roberts and Pierce, 1967, and Dill, 1968; in Swift, 1969). The sands and gravels on the shelf could clearly not have been transported seawards over the modern mud belt on the inner shelf, and since modern erosional forces are probably inadequate to have eroded the phosphorites of the middle shelf, these deposits must reflect erosional processes of a lowered sea level. As Late Tertiary downwarping has lowered most of the shelf below the influence of Quaternary fluctuations in sea level, the glauconite and phosphorite must be products of a Tertiary regression/transgression cycle. Such a regression has been postulated by Dingle (1971) to account for a Late Tertiary outer shelf erosion surface. The retreating and then advancing sea would have eroded the shelf substrate and winnowed the fine sediments seaward, leaving the coarser components behind as a residual deposit.

Although the Tertiary glauco-phosphatic rocks are clearly the source of the authigenic minerals, the origin of the well-sorted, very fine quartzitic sand on the upper slope west of Cape Town is not so obvious (Fig.II-3). These sediments have a minor glauconite component which is probably also derived from the glauco-phosphatic rocks (Birch, 1971). Phosphorites have a subordinate very fine sand and silt-size quartz constituent (see Chapter IV) and it

is suggested that during the major Late Tertiary transgressive/regressive cycle (Dingle, 1971) the very fine quartz was eroded from the underlying strata and transported seawards leaving behind the coarser and denser glauconite and phosphorite sands as a lag deposit (Fig.II-20). Additional very fine quartz may also have been supplied to the outer shelf by fluvial processes. Slumping of this sediment has possibly caused scarring of the slope off Cape Town.

Well-sorted, very fine quartz sand also mantles the shelf off Bokpunt and the inner shelf north of the Olifants River (Fig.II-20). The Olifants River Delta, like that of the Orange River Delta (Rogers, 1973), is mainly composed of this size fraction, and so too is the entire shelf off Lüderitz (Rogers, 1973). The sediment to the north has tentatively been correlated to Pleistocene sedimentation (Rogers, in prep.(a)) and this age can probably be inferred for the sand seawards of the modern mud belt to the south as well. However, the mechanism whereby vast accumulations of very fine sand are concentrated is obviously an important process in the sedimentology of the west coast. The cause of this distinctive textural character is possibly twofold, ie. sediment fractionation (Swift, 1974), or a supply of predominantly unimodal sand to the marine environment (Rogers, in prep.(a)).

Rogers (in prep.(a)) has traced a source of the Orange River detritus to the Beaufort and the Cave Sandstone Groups which are dominantly composed of very fine quartz sand. Although no studies have been made of the sediment size comprising argillaceous rocks in the catchment area of the Berg and Olifants Rivers, it is possible that sediments of the Karoo Supergroup, particularly the Ecca Group, also contain mainly very fine quartz.

Shelf sediment transport is presently a topic of intense interest and a great deal of new data has recently become available. There are clearly two schools of thought on the subject. One group maintains that very little bedload transport occurs seaward of 30 metres, but a second group, 'the catastrophics', believe that considerable movement is possible during 'rare events' (Swift et al., 1971; Sternberg and McManus, 1972 and Komar et al., 1972). Recent field studies of sand movement on the Oregon coast have revealed that very fine sand can be transported as suspended load during severe storms (Smith and Hopkins, 1972). At other times this material moves much slower as bedload, and like coarse sands is entrained by wave-driven bottom currents which have a nett landward direction (Komar et al., 1972).

Late Tertiary downwarping of the continental margin by at least 150 metres (Dingle, 1973(a) and Rogers, 1972) has deepened most of the mid and the outer shelves beyond the influence of Pleistocene regressions/transgressions. Nevertheless, if a maximum sea level low of -140 metres is assumed for the end of the Pleistocene (Guilcher, 1969), then the shelf, to a depth of approximate-

SOME TEXTURAL, MINERALOGICAL AND CHEMICAL PARAMETERS ALONG TWO TRANSECTS ACROSS THE CONTINENTAL MARGIN

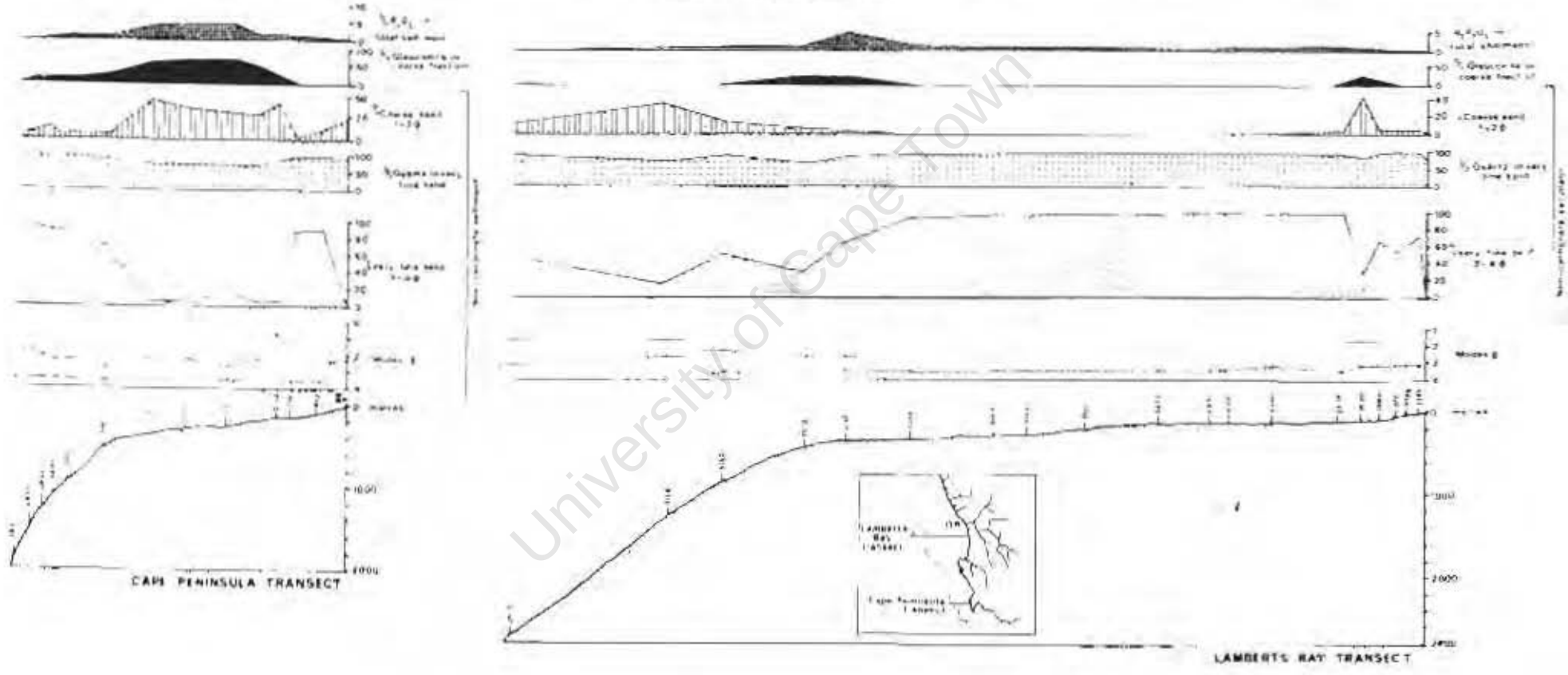


Figure II-20

ly -170 metres, can be expected to have been affected by the fluctuations of sea level. During repeated regressions/transgressions, silt and clay, and perhaps very fine sand, if it can be transported in suspension, would have been winnowed seawards beyond the 170 metre isobath.

On commencement of the Flandrian transgression the coastline would have moved rapidly over the flat-lying inner shelf until it reached the base of the rocky platform at about 100 metres. As the shoreline advanced more slowly up the steep gradient, fine sediment was able to settle out over the quartzitic sands deeper than 140 metres.

2.9.2. Holocene sedimentation.

A dearth of quantitative data on currents, especially on the inner shelf, and of terrigenous influx into this area means that interpretation of sedimentary processes can only be speculative. However, the Olifants and Berg Rivers, because they drain extensive areas of mainly argillaceous rocks and because of their high discharge rates (see Chapter I), can be expected to contribute a major proportion of sediment reaching the coast. A thick lens of terrigenous mud at the base of the coastal platform between the Berg River and Hondeklip Bay is evidence of this influx.

River sediment input is partly controlled by river mouth geometry (Swift, 1969). River mouths off the South African coasts are drowned because they have not yet recovered from the rapid post-Pleistocene sea level rise. Estuaries tend, therefore, to be still-water settling basins (Swift, 1969), where sediment bedload is dropped owing to a sudden change in water velocity. Once the suspensive and tractive loads have separated, the two fractions proceed through the sedimentary cycle on separate paths. Estuaries can also act as a trap for coarse sediment moving along the beach by long shore drift. The transport of sand in the littoral and coastal regions between Hondeklip Bay and Sylvia Hill is the subject of detailed studies by Rogers (1975 and in prep.(b)). The west coast is exposed to large southwesterly swells which are generated over an extensive fetch across the South Atlantic Ocean and which meet the shore obliquely giving rise to a strong northward longshore drift. Wave action confines the coarse sediment to the coast. The sand continues to move northward until a south-facing bay or estuary is encountered. Here the wind dries the intertidal sand and blows it ashore. Extensive areas of vegetated dunes inland from the Swartlintjies River indicate that this process was more active in the Pleistocene than it is today. The presence of blown sand on the north bank of river mouths implies that the process is still operative, albeit subdued. Unfilled and partly filled hollows and depressions on the coastal platform immediately off shore indicate that little coarse sediment is actually reaching the sea in the present day (O'Shea, 1971).

Under present conditions suspended material is clearly escaping the shore and accumulating at the base of the coastal platform. This deposit can be classified "nearshore" mud according to the terminology devised by McCave (1972). There are possibly two mechanisms whereby this deposit is being maintained. The one is by shoreward advective transport (transport of suspended material owing to net horizontal water movement) resulting from the intrusion of colder bottom water owing to upwelling (McCave, 1972) or during severe floods when there is often a net shoreward movement of bottom water (referred to as a "salt wedge", Swift, 1969) in response to seaward motion of lighter fresh surface water extruded from rivers. This would prevent the bottom nephaloid layer from prograding across the shelf and once deposited in a belt at the base of the coastal platform, the mud may develop sufficient cohesiveness to withstand stormy periods (McCave, 1972).

The fine sediment seaward of the main mud belt at the foot of the coastal platform could either be generated by unmixing of the Pleistocene sediments (autochthonous) or could be supplied by present-day river processes (allochtonous)(Swift, 1969).

Although mud blankets rarely extend beyond 30-40 kilometres from the shore (Curray, 1965), many mid-shelf sands show evidence of limited mixing of recent fines with relict-sand populations (Curray, 1969; McManus et al., 1969 and Swift et al., 1969). A process of diffusion, involving repeated deposition and resuspension, provides a mechanism for enlarging the mud belt and progradation of fine sediments. Although high level escape of mud is not generally considered important, Drake et al. (1972) have found that suspended particulate matter may be transported across the shelf in the presence of thermal stratification within the water column. Under these conditions suspended sediment can become detached from the near-bottom nephaloid layer and moved offshore at all levels, until collapse of the stratification causes the deposition of clays and silts over the middle shelf. The origin of the terrigenous mud on the mid and the outer shelves cannot be determined beyond doubt with the data at hand. However, a gradual decrease in mud abundance seawards and moderately high inorganic concentrations (0,25 mg/l) of suspended matter off the Saldanha Bay/Elands Bay region (Emery et al., 1973) favour minor present-day deposition in these off-shore areas. Mud may also have been deposited in quieter water in the wake of the Flandrian transgression and become mixed into the older, well-sorted quartzitic sands (Swift, 1969 and Rogers, 1971). Slow deposition of fines has allowed considerable mixing by bioturbation, current surge or wave action as evinced by the lack of textural stratification in these sediments.

As is the case off the eastern coast of North America (Meade, 1972), biogenic detritus on the continental margin off the Cape coast is as important

as river-derived sediment. The nature and distribution of biogenic sediment has largely been determined by the presence of the Benguela Current and location of the South East Trade Wind Drift (Rogers, 1972). As mentioned in Chapter I, the Benguela Current can be divided into the off-shore divergence belt of subsurface upwelling and the inshore zone of surface upwelling. The bottom sediment in the outer parts of the continental margin north of Saldanha Bay and the slope to the south are characterized by abundant foraminifera. The distribution of zooplankton and coccolithophorids has been linked with the less intense upwelled waters of the offshore divergence which are relatively warm and less saline in comparison with the inshore zone of vigorous surface upwelling and high phytoplankton population (Rogers, 1972). Moderately high concentrations (0,5 mg/l) of organic suspended matter in the waters off the Cape west coast (Emery et al., 1973) and high organic carbon values of the nearshore (7% C_{org}) and outer shelf (2,5% C_{org}) bottom sediment are evidence of the high biological activity in these upwelled waters.

The outer shelf has remained free of fine sediment by turbulence above the shelf break caused by subsurface upwelling (Stander, 1964), and possibly by internal waves (Defant, 1961) and the northward flowing Benguela Current (Van Andel and Calvert, 1971 and Bang, 1973(b)). The absence of mud on the shelf off the Cape Peninsula and west of Saldanha Bay is probably due to a limited source area and to turbulence associated with upwelling in the Cape Point Valley and the Cape Canyon, respectively.

The sedimentary history of the surficial sediments is, therefore, complex, but can be seen simply in terms of a Late Tertiary regression/transgression which gave rise to residual mid-shelf glauconite and phosphorite deposits, and to Quaternary sedimentation, dominated by inshore terrigenous deposition and off-shore biogenic activity associated with the zone of divergent subsurface upwelling.

CHAPTER III. THE CLAY FRACTION (<2μm)

3.1. Introduction

Clays have been studied for many reasons, but perhaps the most fundamental problem that has confronted the clay petrologist is whether clay minerals in the basin of deposition are basically "detrital" in nature or whether diagenesis has been sufficiently intense to mask the characteristics it inherited from its source area. Seaward changes in mineralogy led some workers (Grim et al., 1949; Grim and Johns, 1954; Powers, 1957 and Millot et al., 1963) to conclude severe structural and chemical changes in the depositional environment. In more recent studies (Weaver, 1958(a) and (b), 1967 (a); Taggert and Kaiser, 1960; Griffen, 1962; Hofmeyer, 1971; Gillott, 1971 and Morton, 1972) areal changes are attributed to variations in source and current dispersal and it is now realized that seaward transitions are intensified by differential flocculation of clay minerals in the marine environment (Van Andel and Postma, 1954; Whitehouse et al., 1960 and Porrenga, 1967).

Numerous clay mineral investigations have also been made to aid provenance and dispersal studies, particularly adjacent to large rivers (Porrenga, 1966; Siegal et al., 1968; Kunze et al., 1968; Scafe and Kunze, 1971; Fleischer, 1972 and Shaw, 1973).

A great deal of geochemical research has been done on shallow water materials to establish mechanisms by which elements are incorporated into the sediment (Hirst, 1962(a) and (b); Gad et al., 1969; Curtis, 1969 and Till, 1970). Multi-element analyses coupled with statistical reduction have aided provenance and dispersion studies (Spencer, 1966; Spencer et al., 1968; Hirst and Kaye, 1971 and Catt et al., 1971) and helped to explain how the geochemistry of sediment is controlled by mineralogy and texture (Hirst, 1962(a); Billings and Ragland, 1968; White, 1970; Summerhayes, 1970 and Naido and Hood, 1972). Trace elements have also been used with limited success as salinity (Kieth and Degens, 1959 and Thompson, 1968) and depth indicators (Kieth and Degens, 1959; Curtis, 1964 and Nicholls, 1967).

Brongersma-Sanders (1957, 1966, 1968 and 1969) proposed that many shale deposits were enriched in metals by the death and decay of vast numbers of plankton in areas of oceanic upwelling. The authoress explained the metal enrichment in the Permian Kupferschiefer sediments of north Germany using this model and recently Calvert and Price (1970) have applied the model successfully to explain the origin of the organo-metallic diatomaceous muds off South West Africa. Calvert and Price (1970) worked in an area of vigorous upwelling off Walvis Bay,but intense periodic upwelling cells also exist in the area presently being studied (Hart and Currie, 1960 and Bang, 1971 and 1973(a)).An aim of this investigation is therefore to determine the influence upwelling has on the metal content of the surficial sediments.

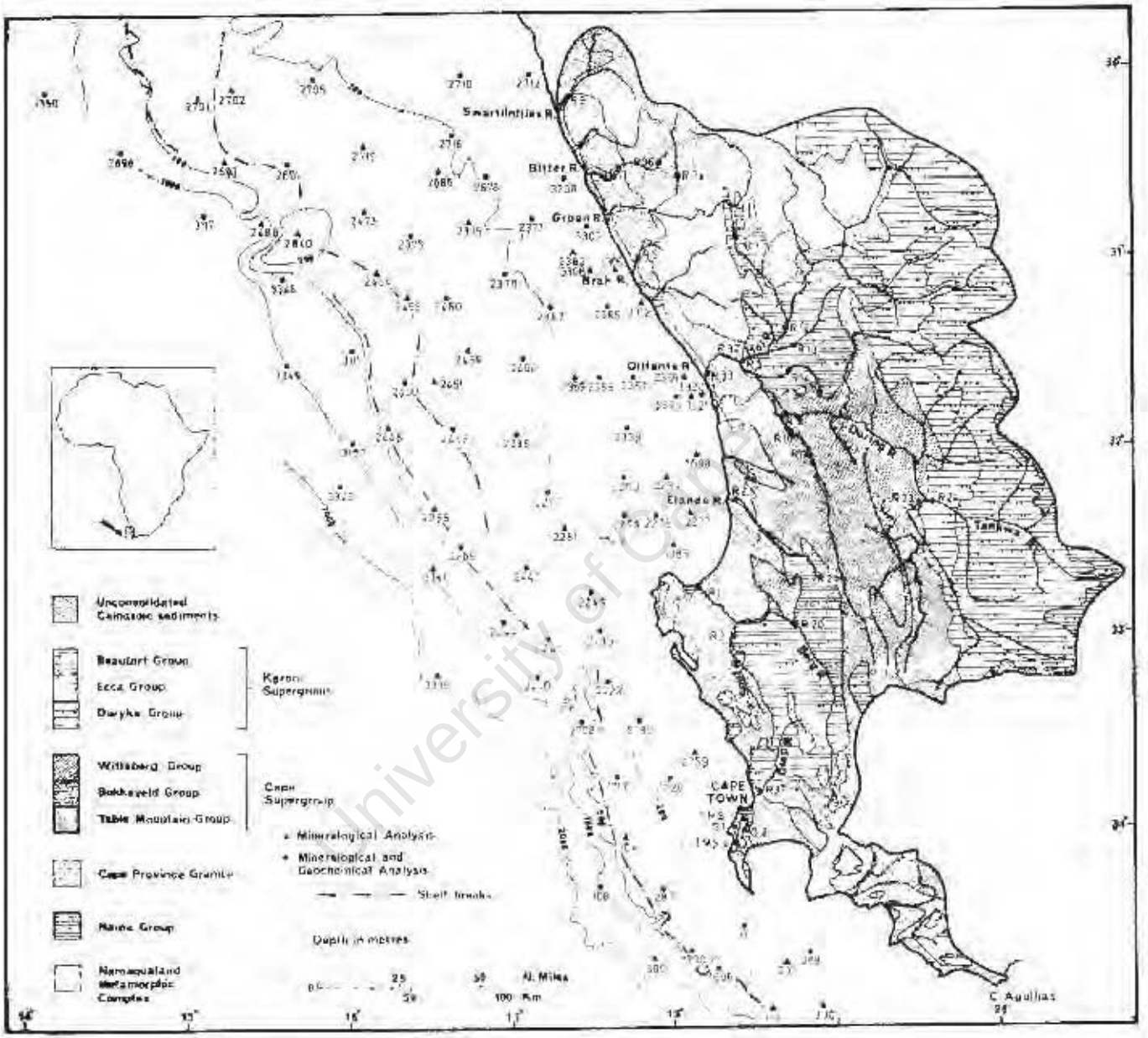


Figure III-1

Authigenic minerals, especially glauconite and phosphorite, are abundant on the south-west African shelf. As diagenesis predominantly involves the clay component, a study of the mineralogy and geochemistry of this fraction could help to explain the variations that have been observed in the nature and abundance of these authigenic minerals.

The regional geology of the drainage area adjacent to the continental margin under study varies markedly. Metasediments of the Namaqualand complex lie north of the Olifants River, and sandstones, quartzites and shales of the Cape, Nama and Karoo Groups and Supergroups, as well as minor granites are found to the south. The climate likewise changes from a mediterranean type, with moderately low precipitation (400 - 1000 mm/yr) in the south to a semi-arid regime (100 - 700 mm/yr) north of the Olifants (Schulze, 1965). As the character of clay minerals is largely dependent on the geology and climate of the source area (Milne and Earley, 1958; Barshad, 1966 and Johnson, 1970), it is also important to determine the influence onland variations exert on the adjacent marine sediment. A comprehensive investigation (Danchin, 1970 and Hofmeyer, 1971) of the shales in the drainage area has provided valuable geochemical and mineralogical information regarding the source material for the continental margin sediments.

3.2. Clay mineralogy

3.2.1. Introduction.

Sediment from the western Cape shelf contains between 0 and 80% clay-size material (<4μm) and the average clay content for all samples analysed is over 17%. The fine fraction therefore constitutes an important portion of the sediment on the continental margin.

The clay minerals mentioned in this work eg. illite, kaolinite etc. are not specific mineral names, but are terms used in a colloquial sense to designate a group of minerals and no attempt has been made to identify specific mineral species.

3.2.2. Analytical methods.

Ninety-two marine samples (Fig.III-1) were initially dialyzed to remove interstitial salt and subsequently separated into <2μm; 2-15μm; 15-60μm fractions by repeated sedimentation using distilled water and no deflocculent. Biogenic carbonate was dissolved using 25% glacial acetic acid and organic carbon was oxidized with 30% hydrogen peroxide. Sixteen river samples were similarly separated into <2μm; and >60μm fractions, but were not pretreated.

Two oriented slides were prepared for each sample by pipetting a magnesium-saturated clay suspension on to glass slides with an eye-dropper and drying it rapidly under a flood lamp at less than 50°C. One slide was

initially diffracted untreated, and subsequently again after heating to 550°C for one hour, whereas the other slide was glycolated prior to diffraction. Clay minerals were identified by their characteristic basal reflection maxima and their proportions were semi-quantitatively estimated by weighting the integrated peak areas (Johns et al., 1954) on glycolated diffractograms.

Results of these mineralogical and geochemical analyses and a description of the methods employed are reported in full in Appendix III, along with a discussion of problems encountered in the collection, preparation and analysis of clay samples.

3.2.3. Areal distribution.

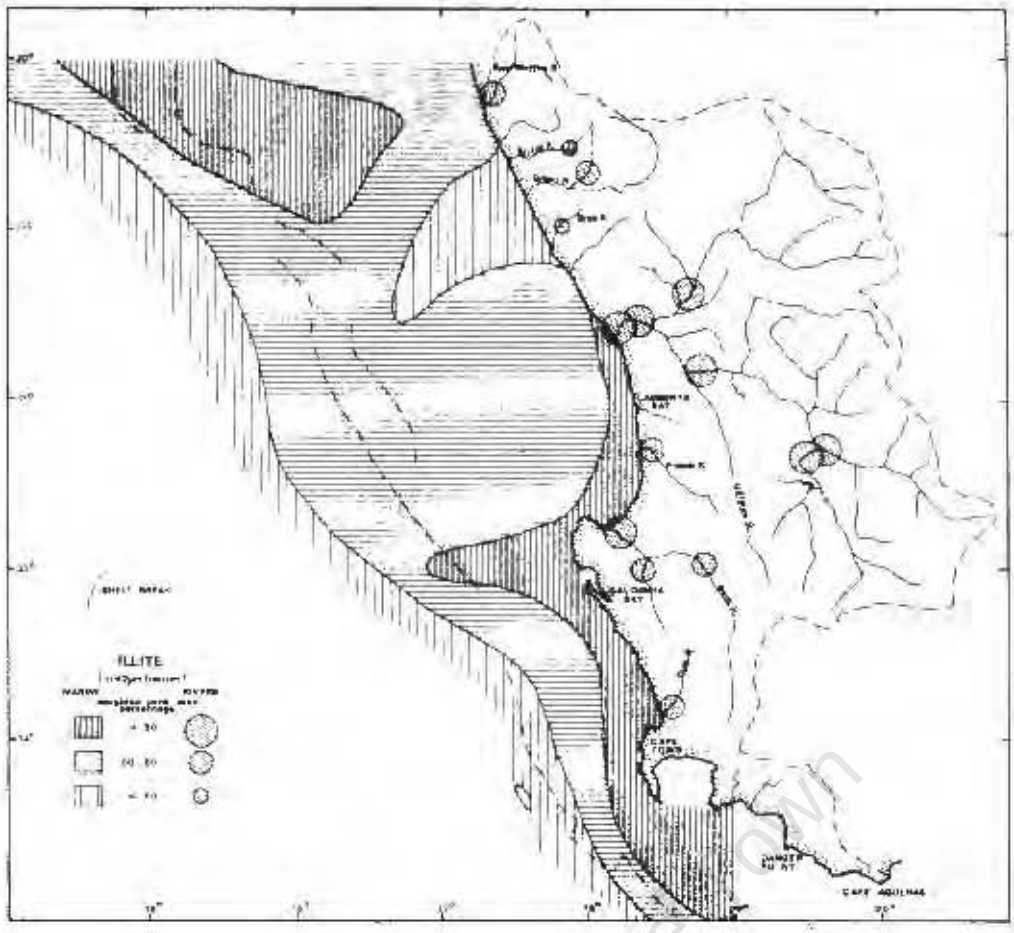
(a) Clay minerals in the <2μm fraction.

The distribution of marine clays is characterized by an overwhelming abundance of illite (Fig.III-2). South of the Olifants River, illite shows a clear seaward depletion across the shelf, and although this trend is also evident to the north as well, it is complicated by a slight mid-shelf enrichment and moderately reduced values in the nearshore region off the Bitter River. The illite concentration decreases from 90% near the coast to 50-60% on the slope.

Illite is also the most dominant clay mineral in the river sediments, but the Olifants River and its tributaries which drain the argillaceous sediments of the Karoo, Nama and Cape Groups and Supergroups are distinctly enriched in illitic clays compared to other rivers.

The distribution of montmorillonite (Fig.III-2) shows the reverse trend to that of illite. The concentration of this mineral clearly increases seawards, generally from less than 10% in the nearshore sediments to 20-30% on the slope. Anomalously high montmorillonite occurs on the inner shelf of the Groen River. This deposit of montmorillonite-rich clay is responsible for the apparent paucity of illite off the Namaqualand coast (the shore bordering the Namaqualand metasediments) mentioned previously, and the slight depletion of montmorillonite on the outer shelf in the north is related to a marginal enrichment in illite.

River clays are notably depleted in montmorillonite. No detectable quantities of this mineral were found in rivers draining the region to the south, but minor (6%) quantities occur in the tributaries of the Olifants River which erode sediments of the Nama Group and the Karoo Supergroup. This is not surprising since these argillaceous rocks are known to contain subordinate amounts of montmorillonite (Danchin, 1970 and Hofmeyer, 1971). The contribution of montmorillonite from the Namaqualand metasediments is difficult to assess. Values are generally low, but one sample from the Bitter River contains more than 20% of this mineral.



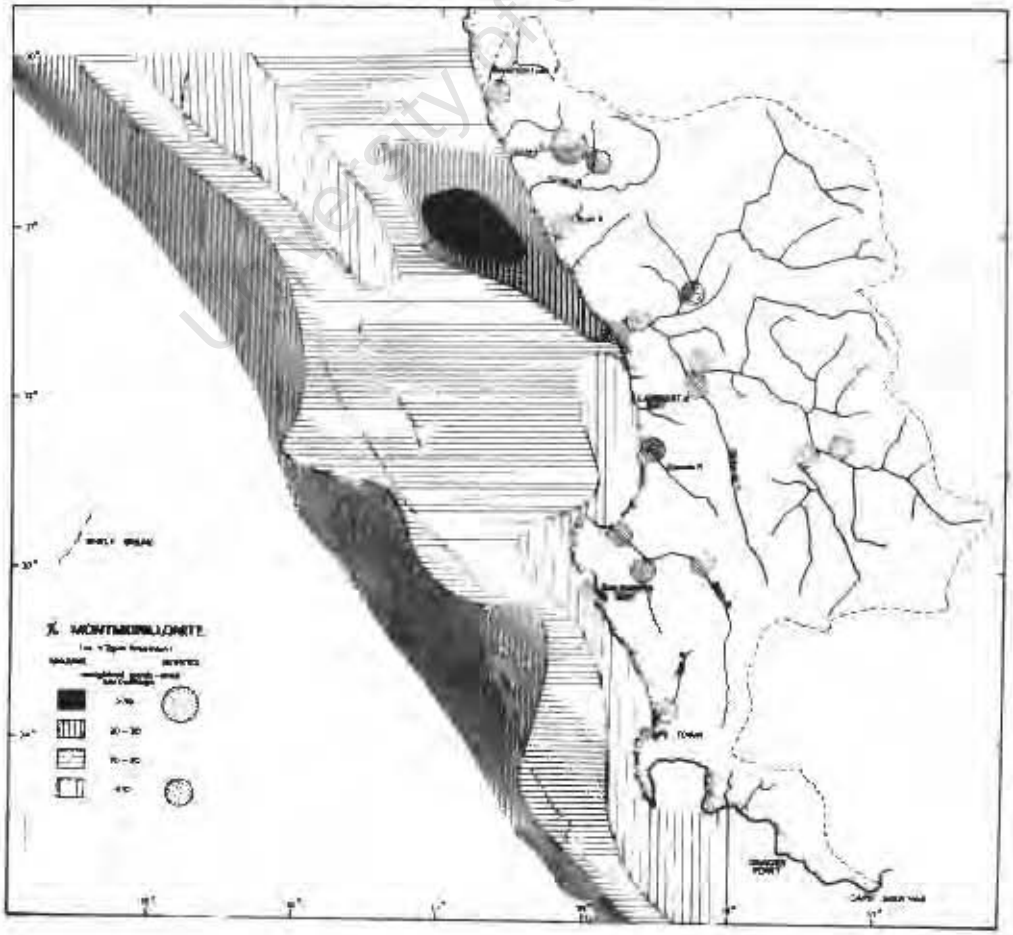
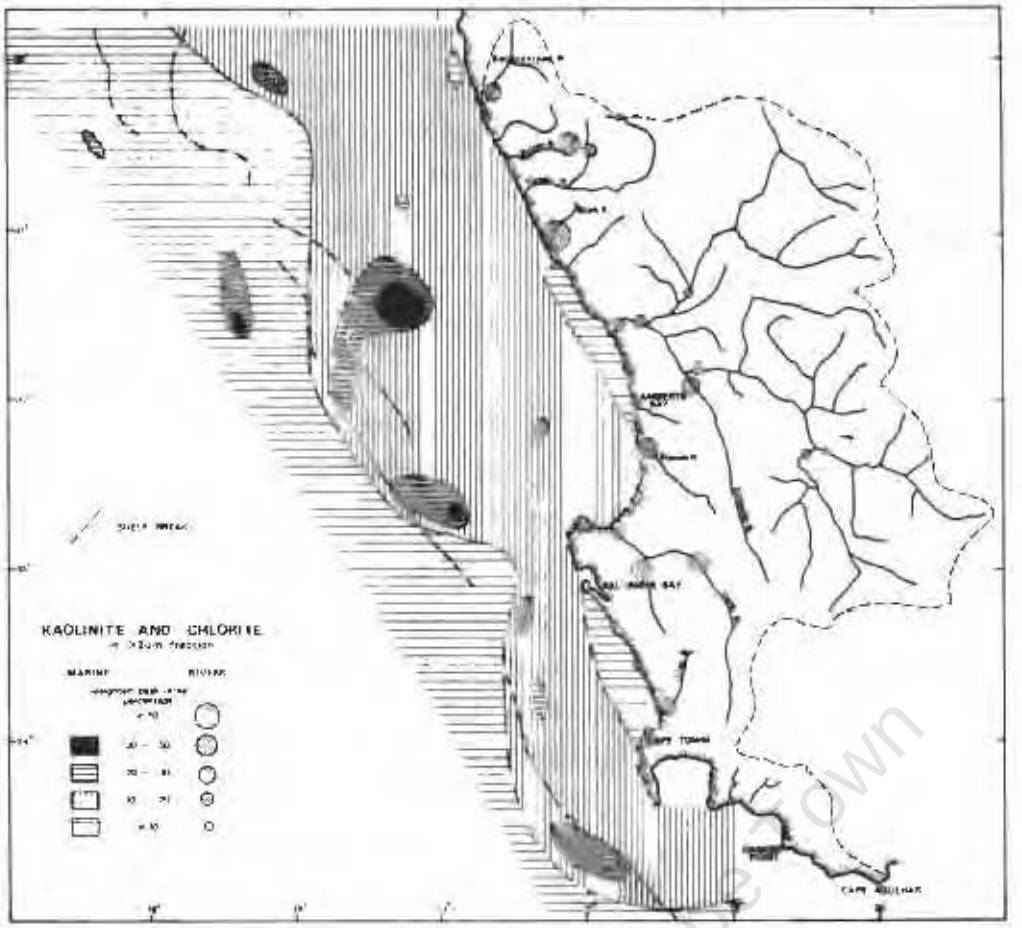


Figure III-2



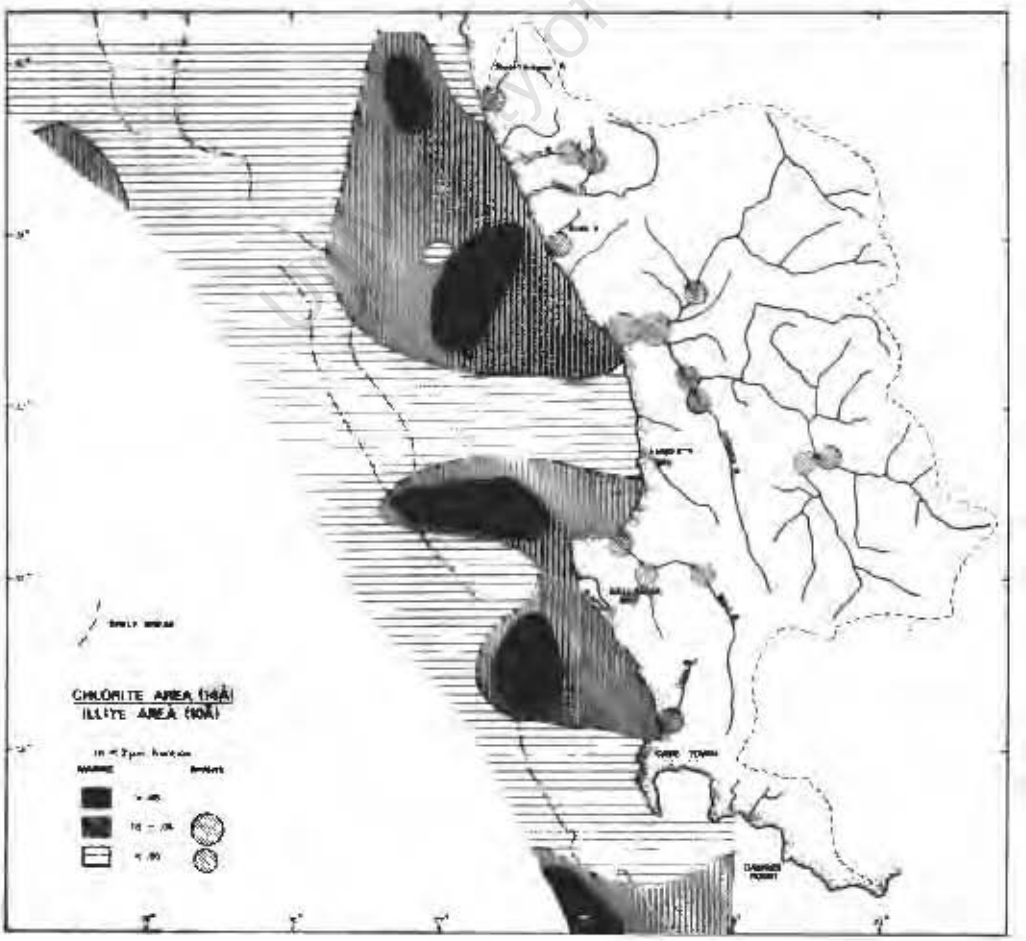


Figure III-3

Because chlorite was only present in minor quantities, kaolinite and chlorite have been presented on an undifferentiated basis in Figure III-3. In contrast to montmorillonite which increases seawards and illite which increases landwards, kaolinite tends to be most concentrated on the outer shelf. Values of approximately 5-10% are found on the slope and nearshore regions, and mid-shelf concentrations are between 15 and 20%. A moderately developed zone of enrichment in the vicinity of shelf break includes values of between 20 and 30%.

The variation in the abundance of kaolinite in the rivers is significant. Clay in the upper reaches of the Berg River and in the Diep River, both of which drain extensive outcrops of Cape Granite, contains more than 25% kaolinite. Rivers draining the Namaqualand metasediments contain clay which is likewise rich in kaolinite, some values exceeding 60% (Brak River), whereas clay in the Olifants River, and especially its upper tributaries (Tankwa River) which drain the Karoo sediments, is markedly kaolinite-poor.

It has been found convenient to assess the chlorite contribution (Fig.III-3) by expressing it relative to illite. The very variable chlorite/illite distribution is difficult to evaluate. High values off the Namaqualand coast occur adjacent to rivers which contain sediment depleted in chlorite, and it appears that only the Olifants River supplies the marine environment with detectable quantities of this mineral. The presence of chlorite in the Olifants River sediments correlates with moderately high chlorite values reported by Hofmeyer (1971) for Nama sediments. Moderate chlorite enrichment occurs off Saldanha Bay as well as south of Cape Point. However, only minor chlorite could be detected in the clays from rivers draining the adjacent onland sediments.

(b) Non-clay minerals in the <2μm fraction.

On the continental shelf alkali feldspar is more common south of the Olifants River than in the north, but plagioclase is almost always more abundant than alkali feldspar. No clear areal distribution trends of feldspar are apparent in the marine clays. The feldspar content of the fine alluvial sediment is, like that of the clay minerals, more variable in the marine environment. Plagioclase was present in all river clays, whereas alkali feldspar occurred in sediment derived from the Bokkeveld and Witteberg Groups (samples R-16 and R-23) and was more abundant than plagioclase in rivers draining the Namaqualand metasediments. The large supply of alkali feldspar to the marine environment north of the Olifants River is not reflected in the feldspar concentration in the adjacent marine sediments. This feature is similar to the distribution of kaolinite in this respect.

(c) Clay minerals in the 2-15μm fraction.

As the <2μm fraction was utilized for both mineralogical and geochemical studies, no deflocculent could be added during the sedimentation process used to concentrate the material. Because of the unknown flocculation characteristics of these clays and since no measurement was made of the particle size being studied, a check was carried out on the coarse clay and fine silt (2-15μm) fraction to assess whether the clay mineral assemblage of the coarser material differed radically from the <2μm clay.

A study of 35 samples indicated distribution trends in the 2-15μm material similar to those observed in the less than 2μm fraction study. The illite and kaolinite concentrations in the 2-15μm material increased at the expense of the montmorillonite component relative to the <2μm fraction. However, the illite abundance increased shorewards and the montmorillonite component increased seaward in a similar fashion to that observed in the <2μm study except that the trends were not as well developed. In addition, the anomalously high montmorillonite concentration off the Namaqualand coast apparent in the <2μm fraction was also discernible in the investigation of the 2-15μm fraction.

3.2.4. Discussion and conclusions

Illite is frequently the most dominant clay mineral present in the marine sediments, mainly because of the high concentration of micas in many rock types and owing to its relative resistance to chemical weathering (Biscaye, 1965). The preponderance of illite in these shelf sediments is clearly related to its abundance in the adjacent onland argillaceous rocks (Hofmeyer, 1971). Estimations made by Biscaye (1965) and Griffin et al. (1968) of illite for the south-east Atlantic coincide well with values reported in this work (>50% and >70% respectively).

The variation in the abundance of the three major clay mineral species across the shelf is perhaps the most striking feature of this study. Seaward changes in clay mineralogy initially led some workers to conclude that structural and chemical changes occurred in the depositional environment (Grim, 1951). It has since been realized that these trends are related to differential settling and that this separation is enhanced by formation of floccules (Whitehouse and Jeffrey, 1955 and Siegel et al., 1968). Whitehouse et al. (1960) have calculated the settling rate of illite, kaolinite and montmorillonite as 15,8, 11,8 and 1,3 m/day respectively. These workers point out that a horizontal flow of greater than 600 cm/sec is required to eliminate the effect of differential transport. This implies that the northward-flowing Benguela Current (30-50 cm/sec, Bang, 1973(b)) could not override the effect of this process. Off the Cape coast illite is most

abundant in the nearshore region, followed by kaolinite on the outer shelf and finally montmorillonite is most concentrated in the slope sediments. This emphasises the importance of differential settling in the distribution of clay minerals off these shores. Although there are considerable changes in the onland geology and climate from north to south in the hinterland, there are no apparent latitudinal changes in the clay mineral assemblage on the adjacent continental margin off the Cape west coast.

The low montmorillonite abundance noted by Griffin et al. (1968) and Biscaye (1965) (<20% and <9% respectively) for the south-east Atlantic is similar to values obtained in this study. However, the occurrence of high montmorillonite values off the Namaqualand coast in the north requires explanation, especially as sediment in the streams draining the adjacent onland metasediments is seemingly montmorillonite-poor. There are three possible sources for this material. It may be associated with a similar montmorillonite enrichment on the inner shelf to the north which is considered to be derived from the Orange River (Rogers, pers.comm.), but the absence of a clear northward continuation of the deposit tends to mitigate against such a source. Montmorillonite originates by the denudation of metamorphic rocks or by alteration of kaolinitic minerals (Meade, 1967). Montmorillonite can also form from serpentinites (Bashard, 1966) or from micas (Kunze et al., 1968) and chlorites (Griffen and Goldberg, 1963) which have been stripped of their potassium. It is therefore possible that the montmorillonite is being derived either directly by denudation of the metasediments or by secondary alteration. Although most of the rivers draining the metasediments are poor in montmorillonite a sample from the Bitter River (R-36) contained more than 20% of this mineral, but, unfortunately, the Groen River, which is an obvious source for the deposit, has not been sampled (a small tributary of the Groen River contains less than 10% montmorillonite). The montmorillonite may also have originated by reworking of the local nearshore Cretaceous outcrop. Some of these clays are associated with light green glauconite which shows a close association with the Cretaceous (Chapter II). The montmorillonite is not as perfectly related to the underlying strata as the glauconite, but this may be expected as the clay would be more mobile. However, the problem cannot be resolved with the data at hand and will remain until further information becomes available.

The most crystalline montmorillonite occurs on the slope and nearshore regions in areas where the mineral is most abundant. A similar feature has been noticed by Bremner(1975(a))for the clays off South West Africa. The reason for this trend is not clear, but it could be due to relatively increased sedimentation on the inner shelf and slope which results in rapid burial of surface sediment and this blanketing effect may prevent alteration

of the clay minerals (Milne and Earley, 1958). In addition X-ray traces produced by Hofmeyer (1971) and Danchin (1970) of the clays from the onland argillaceous rocks have sharp and well-defined reflections in relation to the broad, more diffuse peaks exhibited by the marine material. This implies a decrease in clay crystallinity on entering the marine environment.

Kaolinite is considered to be a low-latitude clay mineral (Biscaye, 1965) and is more abundant in regions undergoing intense weathering under tropical conditions (Milne and Earley, 1958 and Griffin et al., 1968). The semi-arid regime of the Namaqualand area is therefore not favourable to abundant kaolinite formation. Values of 10 to 15% kaolinite off the Cape west coast are slightly higher thanthose reported by Biscaye (1965) and Griffin et al. (1968) for this region (ie. 5-6% and 5-10% respectively).

The low-grade green schist facies of the Namaqualand metasediments occurs close to the coast and contains chlorite, serpentine, epidote and actinolite (Joubert, 1971). Metamorphic rocks are frequently the source of abundant quantities of this mineral (Johnson, 1970) and serpentine minerals which have a kaolinite-type structure have been shown to be a parent material for some kaolinite (Meade, 1967). Another precursor of kaolinite is feldspar (Griffin et al., 1968) which is a major component of the Nama sediments and the Cape Granite. It is therefore not surprising that the rivers draining these sediments contain abundant kaolinite. However, it is significant that no kaolinite enrichment occurs in the nearshore marine sediments off the Namaqualand coast. This is possibly because kaolinite is being transported across the shelf and is accumulating near the shelf break (see Fig.III-3), but this would raise the question of why the montmorillonite which is enriched in the nearshore sediments off the Namaqualand coast is not also being dispersed in a similar fashion. This may support an earlier suggestion that the montmorillonite is being derived by reworking of Cretaceous outcrops, or that kaolinite has undergone alteration (Meade, 1967).

The distribution of chlorite is often reciprocal to that of kaolinite (Griffin et al., 1968) and is most abundant in the high latitudes. Chlorite is a primary rock mineral (mainly metamorphic) and undergoes minor chemical alteration in the sedimentary cycle, whereas kaolinite is a secondary mineral derived mainly from soil-forming processes (Biscaye, 1965).

The maximum chlorite abundance, estimated on assumptions made by Schultz (1964)(see Appendix III), in the marine sediments is less than 3%, which appears to be slightly low in relation to values reported by Griffin et al., (1968) and Biscaye (1965) for this region (<10% and 5-9% respectively). The chlorite occurrence off the Namaqualand coast is probably derived from the onland low grade metamorphic rocks or the Karoo sediments which also contain

chlorite (Hofmeyer, 1971), the moderate chlorite enrichment off Saldanha Bay and Cape Point is possibly related to the chloritic Nama sediments (Hofmeyer, 1971) or to the metamorphics associated with the intrusive Cape Granite.

3.3. Clay geochemistry

3.3.1. Introduction

A voluminous literature on marine sedimentary geochemistry is readily available; however, investigations of the chemistry of the <2µm fraction are rare. Nevertheless, there is evidence that <2µm fraction studies are becoming more popular as indicated by recent investigations of Speeton clay (Yorkshire)(Parker, 1974) and the clay fraction of sediments from the southern Barents Sea (Wright, 1974).

The <2µm fraction was used in this study because in a total sediment analysis it is difficult to allocate the correct element concentration accurately to each of the numerous mineral species present. Kieth and Degens (1959, p.41) state "Chemical analyses of total sediment are much less significant for environmental studies than analyses of separate fractions, because interpretation requires similar material to be compared". In other words the clay fraction of a diatom ooze could be compared to the clay fraction of a glauconitic mud or an organic-rich onland shale, but the total rock analyses are not comparable. Utilizing the same (<2µm) fraction for chemical as well as structural analyses enables a better comparison between the clay mineralogy and geochemistry to be drawn.

The mud fraction (<63µm) of selected samples was also analysed for K_2O and P_2O_5 in an effort to locate areas of glauconite/phosphate authigenesis and to aid in planning the geochemical investigation on the <2µm fraction. A brief report of these data has been included in this section.

3.3.2. Analytical methods.

K_2O and P_2O_5 analyses were made on the mud fraction (<63µm) of selected samples from the continental margin by FOSKOR by the same methods as described in Chapter II.

Eight elements (Al, K, Ca, Fe, Mn, Ni, Zn and Pb) were determined on the <2µm fraction of 61 marine and 10 river sediments by atomic absorption spectro-photometry using a Varian Techtron, Model AA-6 machine. The relative standard deviation of the method was determined by making replicate analyses (5 independent determinations) of one sample for all elements studied. Most of the samples were analysed in duplicate and only those which fell within two relative standard deviations of the mean were accepted.

Before geochemical analyses of the <2µm samples were undertaken it was necessary to establish what contamination by metallic gear occurred dur-

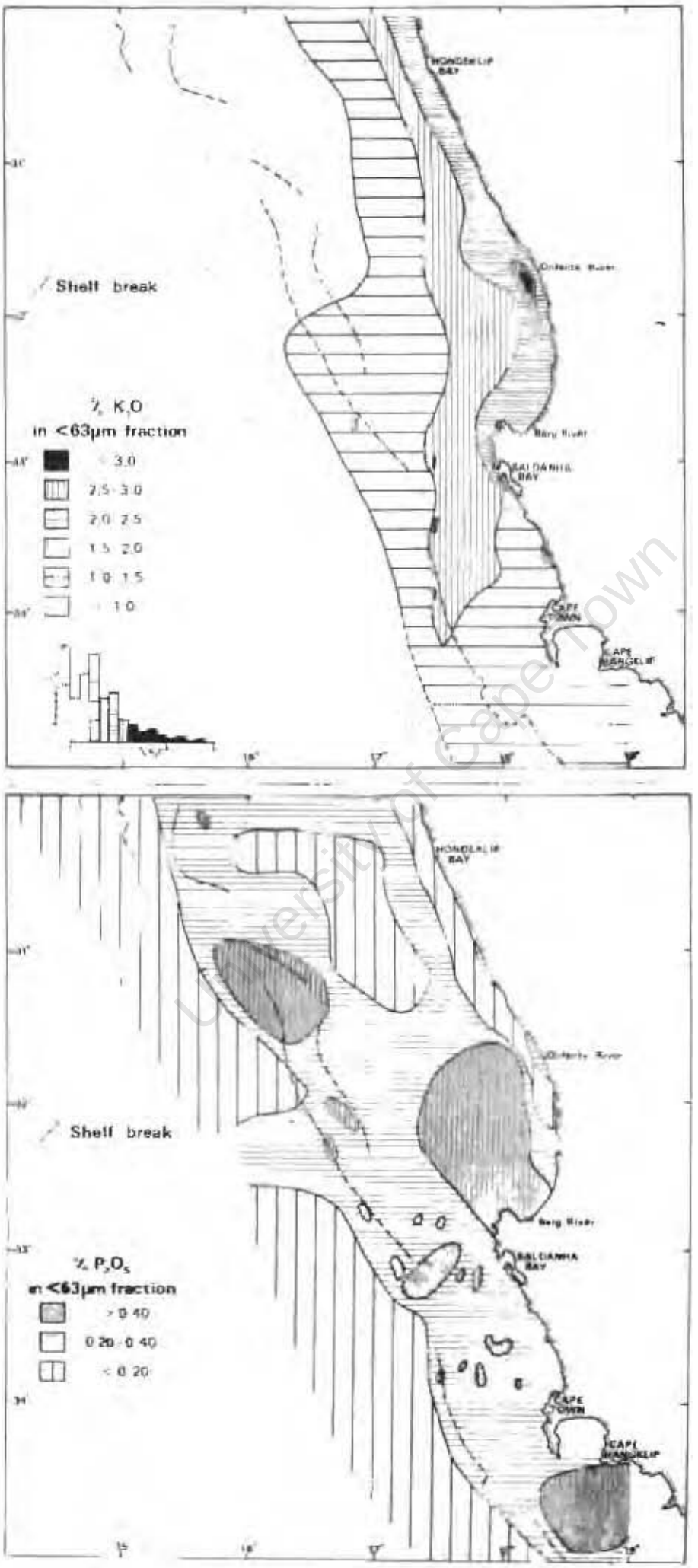


Figure III-4

ing recovery and whether elemental fusion has taken place whilst the sediment was in unfrozen storage. The Mann-Whitney U-test (Siegal, 1956, p.116) was used to test for significant differences among groups of especially recovered and stored subsamples. Significant Ni, Zn and Mn contamination, to the order of about 10% of the elements' concentration in the sample, occurred in sediment collected with the metallic gear, but no significant loss was detected in the unfrozen samples.

Tests were also conducted which established that none of the elements being studied is stripped from clay particles during dialysis.

3.3.3. Areal distribution and inter-element correlations.

The elements determined in the clay fraction fall into 3 groups; these will be discussed together with the geochemical data for the mud.

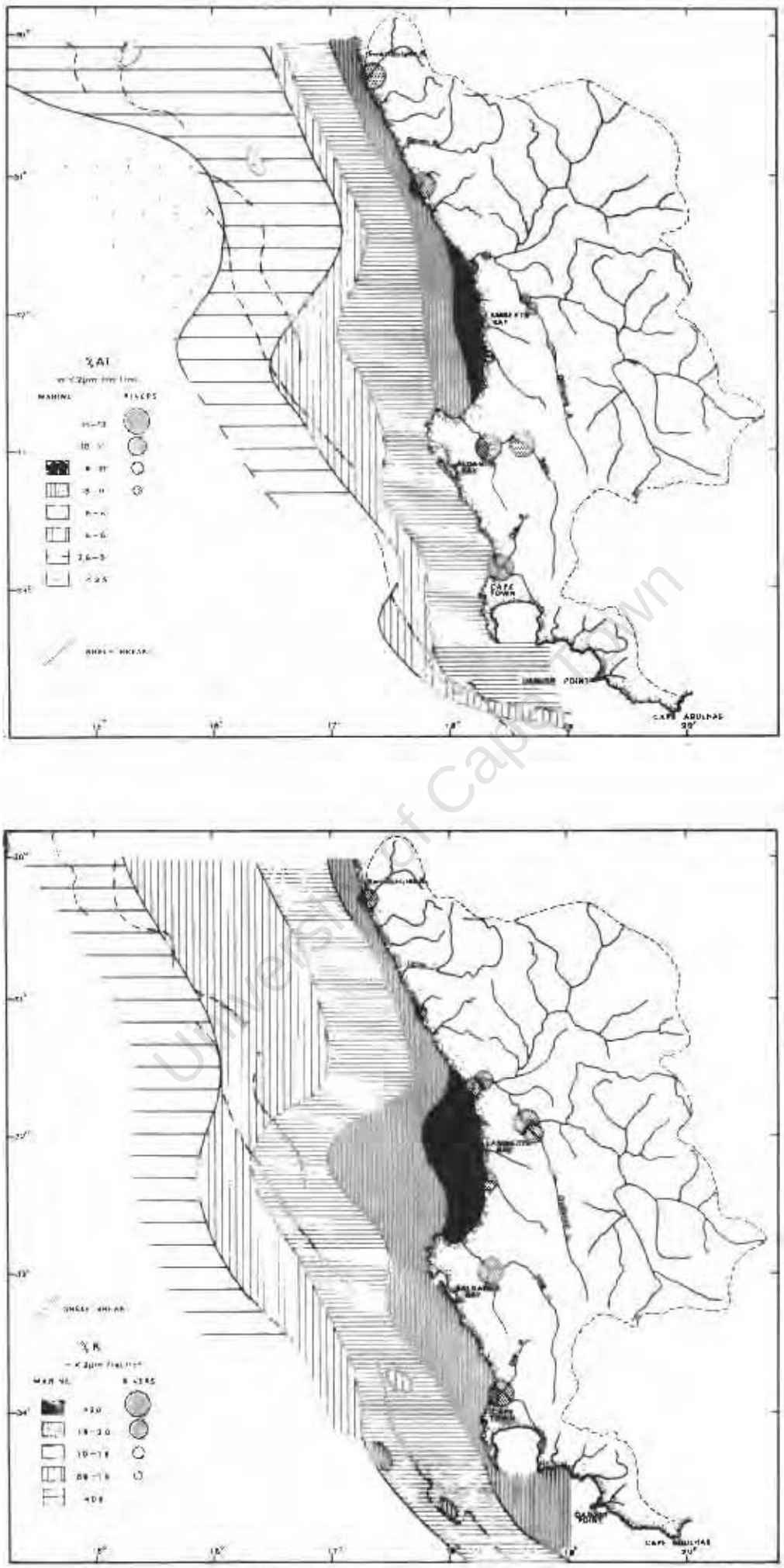
(a) The K_2O and P_2O_5 content of the mud fraction (<63μm).

The K_2O content of the mud fraction is related to the influx of K-rich clays onto the continental shelf (Fig.III-4). In the north the K_2O values decrease rapidly seawards from a maximum directly off the Olifants River mouth. The nearshore faecal pellet muds are rich in K_2O and isopleths show a distinctive westward bulge adjacent to the Berg River. South of Saldanha Bay muds are K-poor, except for a mid shelf 'tongue' of slightly enriched sediments off Cape Town. This pattern is very similar to that of the abundance of mud on the continental shelf (Fig.II-2).

The P_2O_5 content of the mud (Fig.III-4), unlike that of the K_2O, shows no significant distribution pattern, and only a minor variation in its concentration is evident (0,4 to 1,80%). The nearshore faecal pellet muds are poor in P_2O_5 but a slight P_2O_5 enrichment off the Berg River and west of Saldanha Bay is possibly related to increased biogenic activity in regions of upwelling. This would probably also explain the presence of a minor enrichment west of Danger Point as upwelling occurs intermittently in this region.

(b) Al,K, Fe and Mn in the <2μm fraction.

The areal distribution of Al, K, Fe and Mn on the continental margin (Figs.III-5 and 6) is very similar and they are strongly correlated with one another (Fig.III-9). These elements are more abundant in the river clays than in the marine environment, and on the shelf their concentration decreases markedly seawards. They are most abundant in the nearshore region adjacent to the points of maximum terrestial imput, namely the Berg and Olifants Rivers. The isopleths of these elements lie closer to the coast in the north than in the south, probably because a higher carbonate deposition dilutes the shelf sediments towards the north. A strongly negative correlation between Al-K-Fe-Mn group and Ca supports this suggestion (Fig.III-9).



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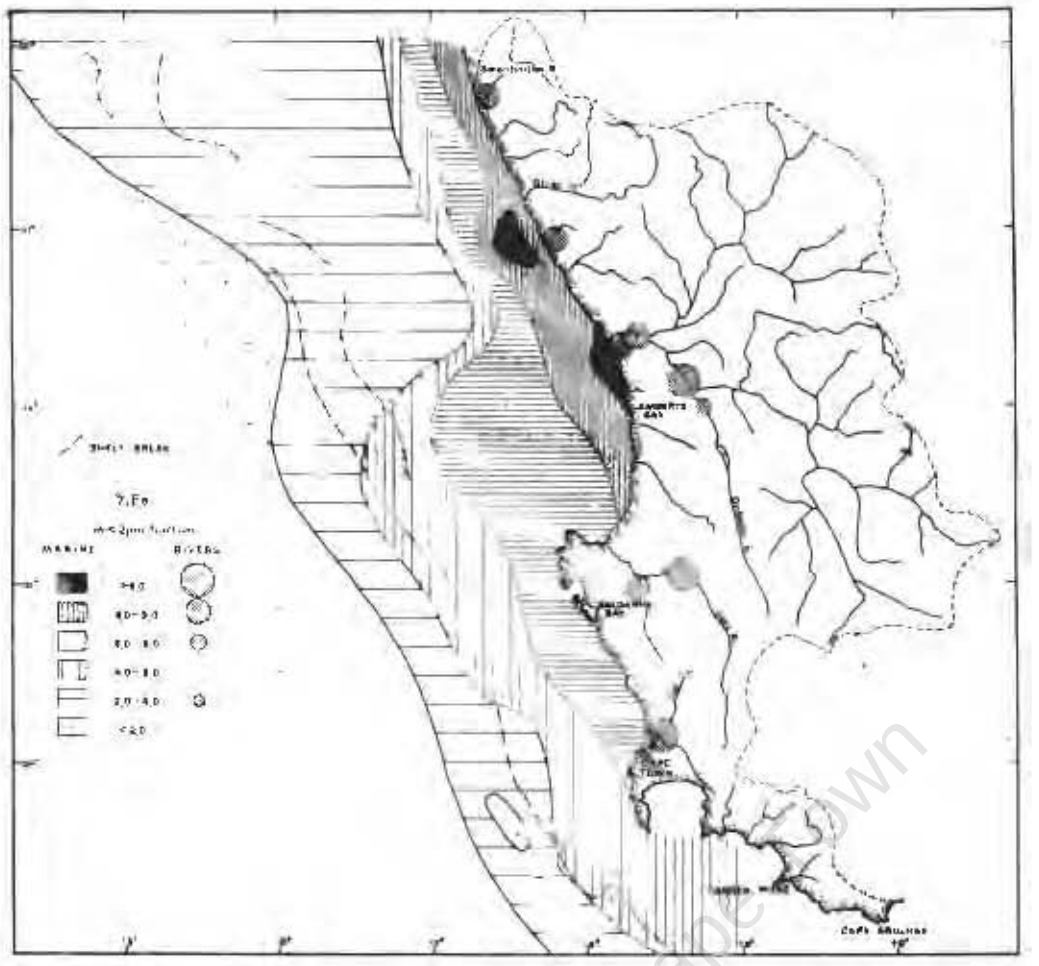
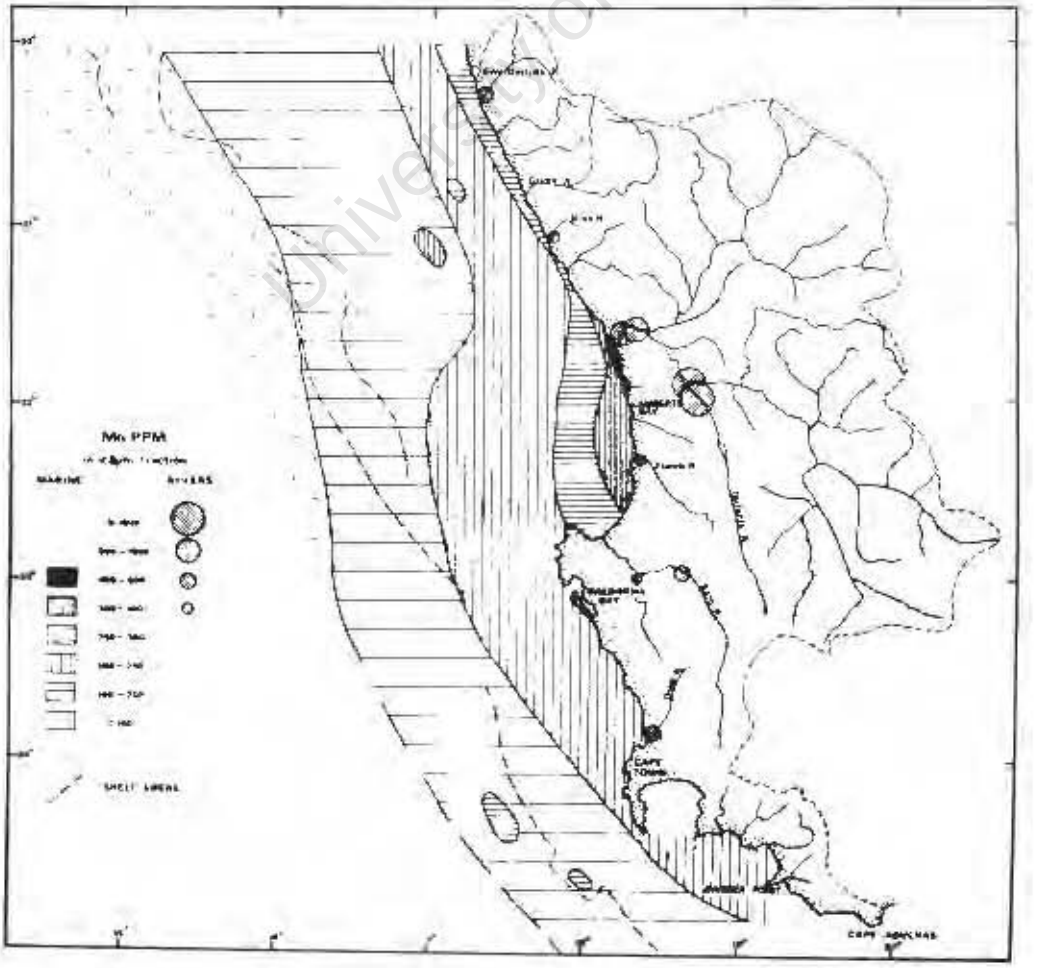




Except for the Olifants River, which appears to be Al-poor and rich in Mn, no major differences in the abundance of any of the above elements is apparent from the other drainage systems. High Mn in the Olifants River clays may be related to the Mn-rich Ecca sediments (Danchin, 1970) which are drained mainly by the Olifants.

(c) Ca in the <2μm fraction.

Ca shows an opposite distribution trend to that of the Al-K-Fe-Mn group of elements (Fig.III-7). This results in a strongly negative correlation between them. Ca is least abundant in the river clays (<1,5%), but increases in abundance markedly seawards from 5% in the nearshore environment to approximately 50% on the slope.

As expected, the areal distribution of Ca in the <2μm fraction follows very closely the distribution of $CaCO_3$ in the total sediment (Fig.III-10). This is exemplified by a very strong positive correlation between the two parameters (correlation coefficient, 909). The shelf clays in the north are Ca-rich and high values are found close to the coast, but west of the Olifants River isopleths turn sharply seawards owing to the influx of (Ca-poor) terrigenous material. Ca enrichment west of Danger Point corresponds to increased carbonate deposition in the form of planktonic foraminifera.

(d) Ni, Zn and Pb in the <2μm fraction.

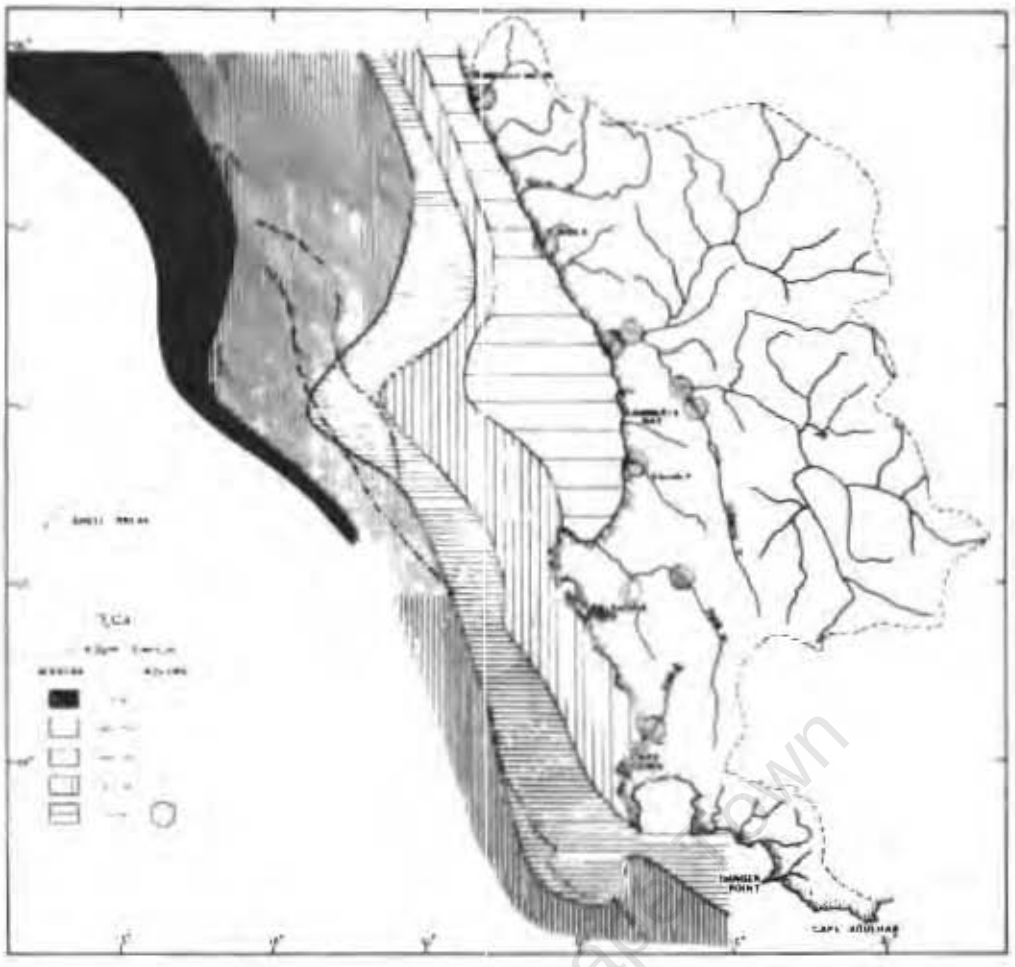
In contrast to the Al-K-Fe-Mn element group, Ni, Zn and Pb are more abundant in the marine environment than in the rivers (Figs.III-7 and 8). Ni, Zn and Pb occur most abundantly in the mid shelf region rather than on the inner shelf, as do Al, K, Fe and Mn. It appears therefore that the distribution of Ni, Zn and Pb is controlled by some mechanism other than terrestrial input.

Ni concentrations are depressed in the highly calcareous slope and nearshore terrigenous muds and occur most abundantly between 30-50 n. miles from the coast. The occurrence of Zn is broadly similar to that of Ni (Fig.III-11), except that because of poor precision, the distribution is more patchy and hence it is only weakly correlated to Ni (correlation coefficient, 395).

Only a preliminary assessment of the Pb distribution could be made because the poor precision in the determinations resulted in very erratic values. Nevertheless using broad contouring intervals, Pb can be seen to concentrate in the mid shelf environment in a similar way to Ni and Zn. Slightly elevated Pb values off the Olifants and Berg Rivers may indicate a minor terrestrial influence, but a large concentration of Pb on the slope appears to be related to the carbonate phase.

3.3.4. Correlation between the geochemistry of the clay and the total sediment (Fig.III-10 and Appendix III-D(i)).

Ca in the clay fraction is very closely related to $CaCO_3$ in the sedi-



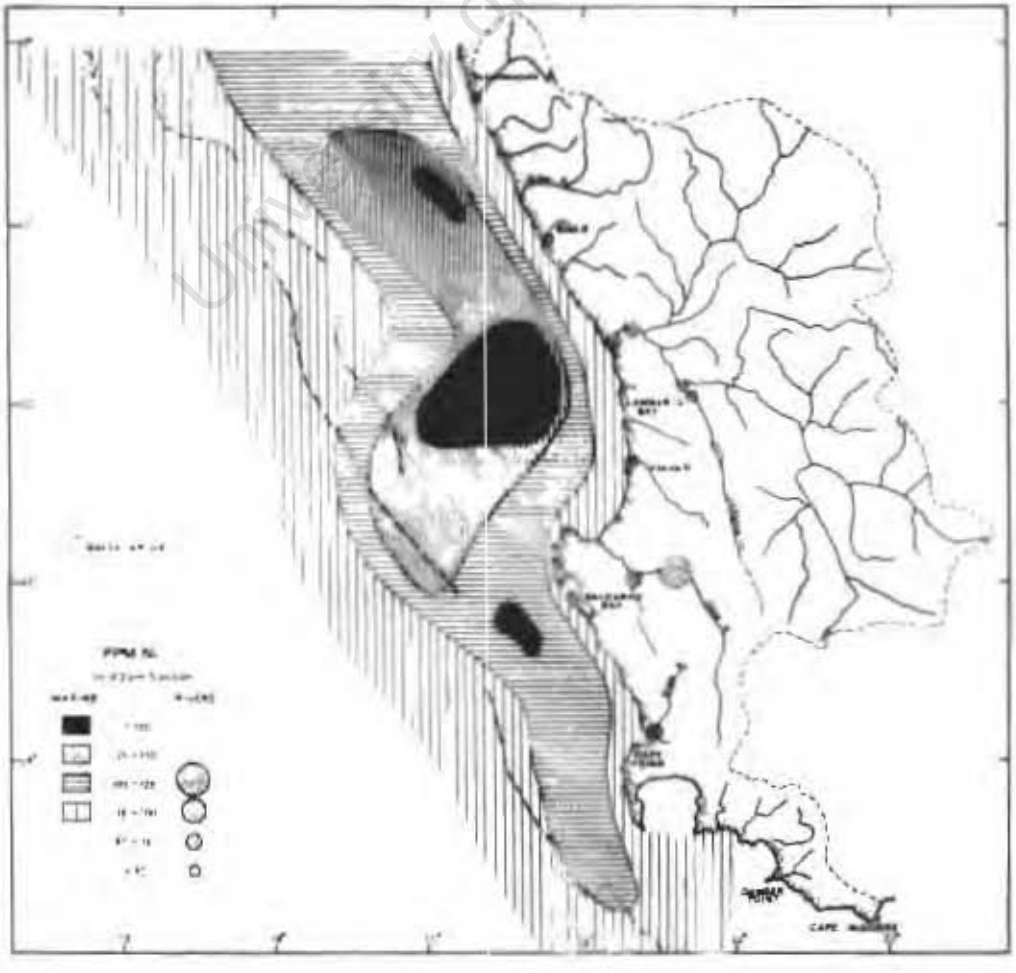
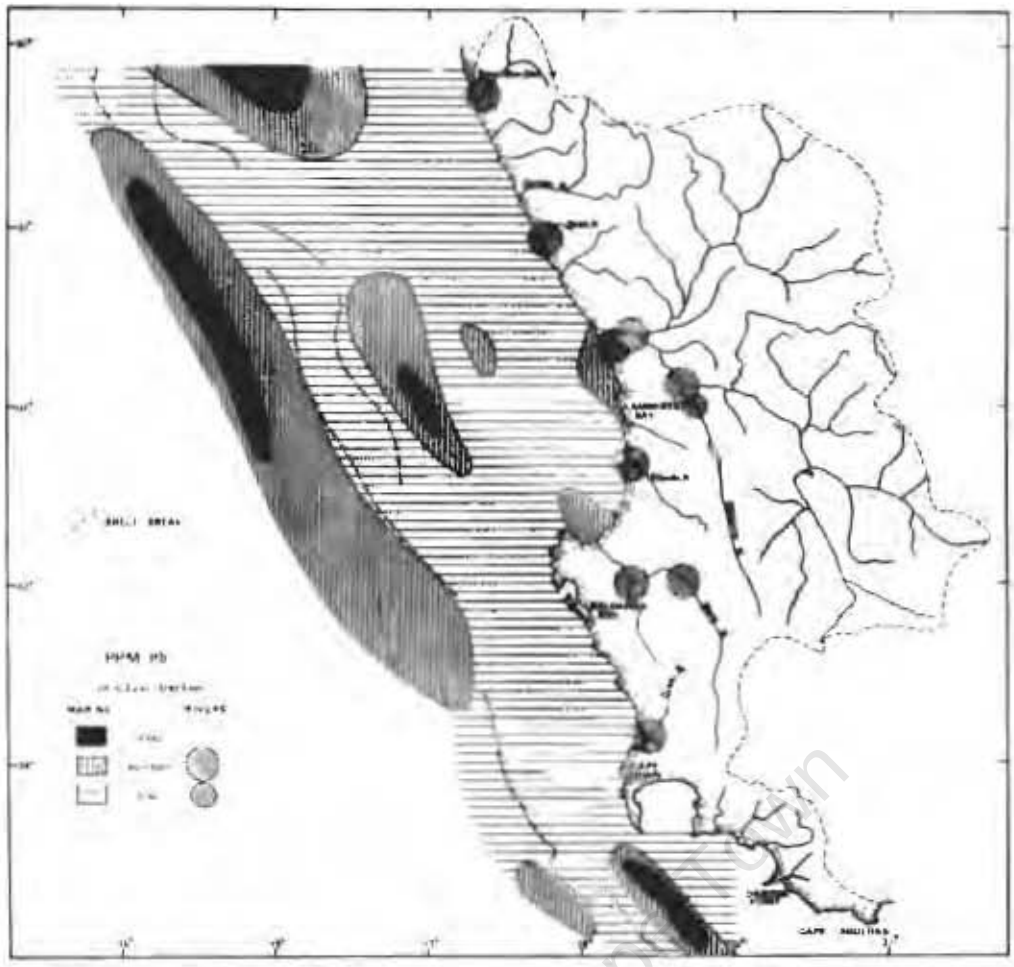


Figure 7



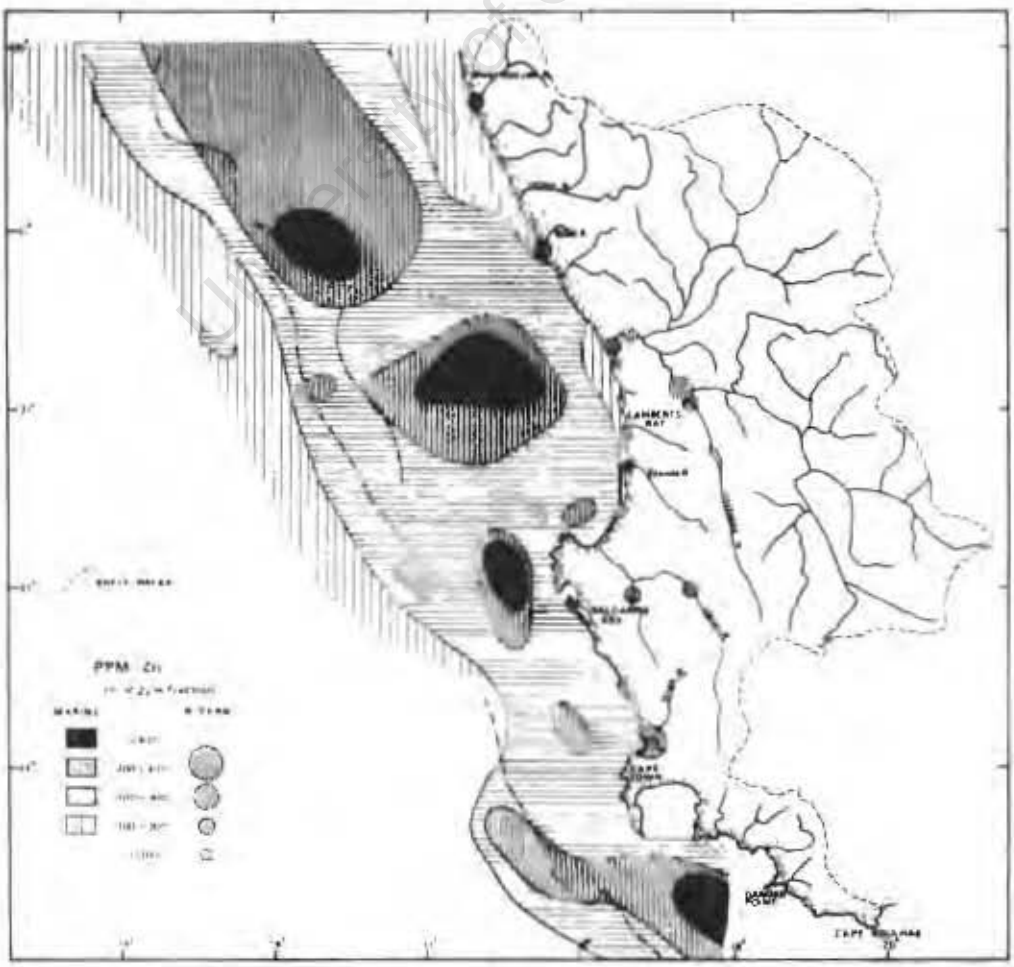


Figure III-8

ment, probably indicating that the Ca in the <2μm material is being derived by breakdown of coarser-calcareous material. A strongly inverse relationship between the Ca (<2μm) and the K_2O in the total sediment is due to excessive dilution of calcareous sediment by K-rich nearshore muds (correlation coefficient of K_2O in the <63μm and <2μm fraction is -,719).

The K_2O content of the mud shows a similar distribution to K in the <2μm fraction, and both are moderately to strongly correlated to the Al-Fe-Mn group. Clearly this is because the distribution of this element in the fine sediment (<2μm and <63μm) is mainly controlled by terrigenous influx, whereas K_2O in the total sediment is dominated by the occurrence of glauconite. This results in a poor correlation between K in both the <2μm and <63μm fractions with K_2O in the total sediment.

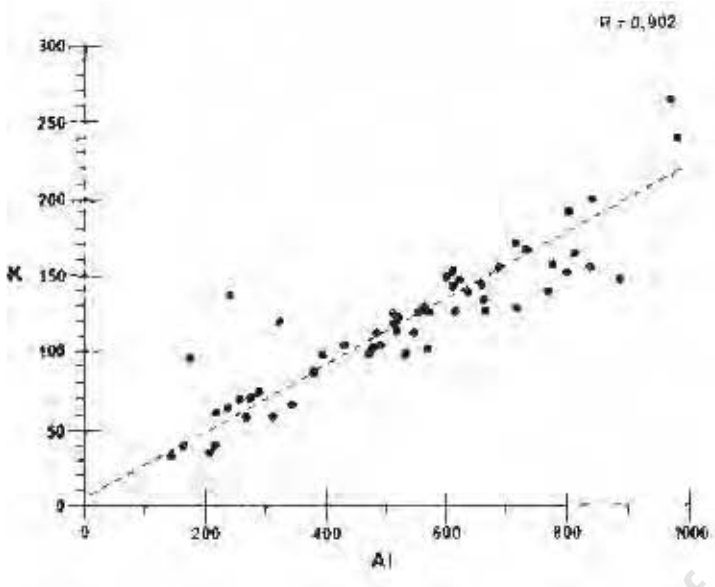
The P_2O_5 contents of the mud and the total sediment are poorly correlated (,248) and neither parameter is even moderately related to abundance of any other (<2μm) element determined. This indicates that P in the marine sediment is not related to terrestrial influx (ie. poor correlation to P_2O_5 with Al-K-Fe-Mn group and low P_2O_5 content of river sediment), nor is P accumulating in significant quantities in the fine fraction in the phosphatic sediment (poor correlation with P_2O_5 in the total sediment) nor in the areas of metallo-organic enrichment (ie. poor correlation with Ni and Zn in the <2μm fraction).

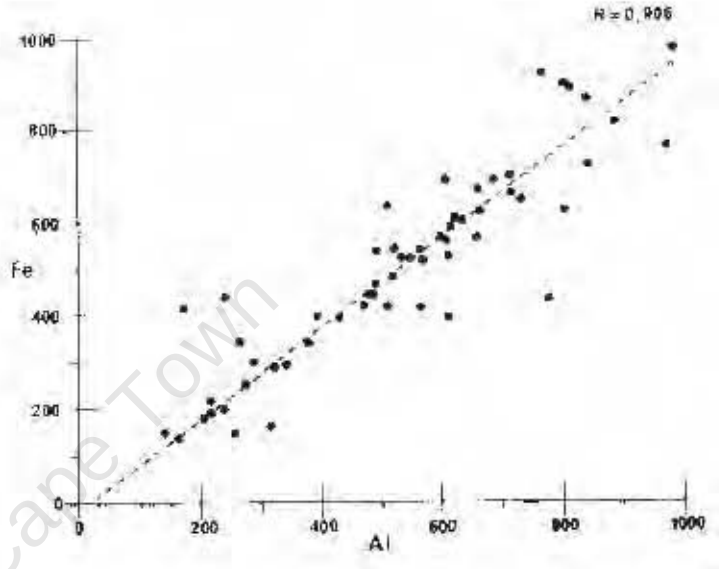
3.3.5. Element partition.

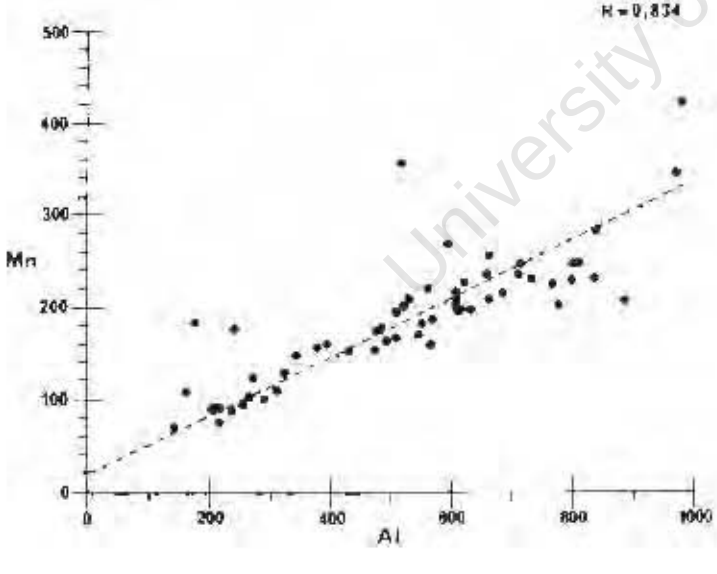
Bulk geochemical analyses of the clay fraction, as reported above, describe the areal distribution of the elements analysed. However, information regarding the partition of these elements would lead to an understanding of the process by which they were incorporated into the sediment.

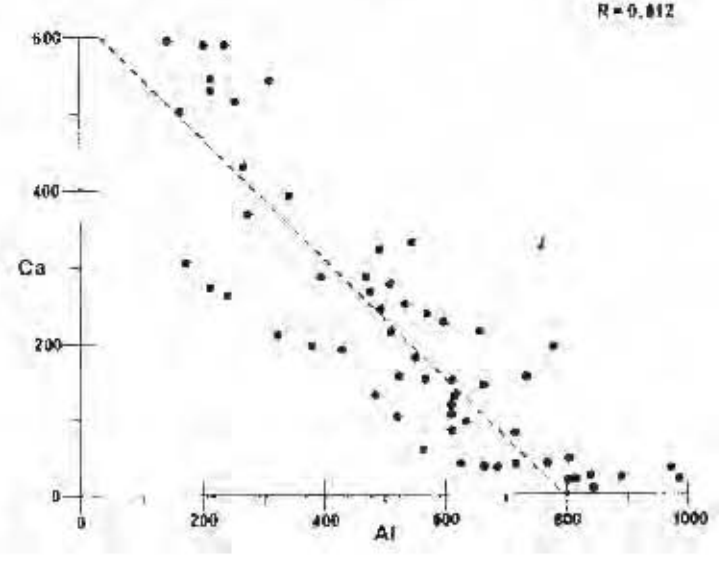
Marine sediment may be regarded as a mixture of material carried into the depositional environment in the solid state and that entering it in solution (Krynine, 1948). Hirst and Nichols (1958) refer to the former as being the "detrital" fraction and the latter as the "non-detrital" component. Elements entering the "basin of deposition" in solution may become incorporated into the sediment by chemical precipitation, adsorption or by biological accumulation (Gad and Le Riche, 1966). But as many analytical problems still exist in separating these fractions (see Appendix III), only a pilot partitioning study was undertaken in an attempt to isolate the most important mechanisms whereby the "non-detrital" fraction is incorporated in the sediment.

Three batches of four samples from the river, nearshore, mid shelf and slope environments were treated with 25% (V/V) glacial acetic acid, an acid/









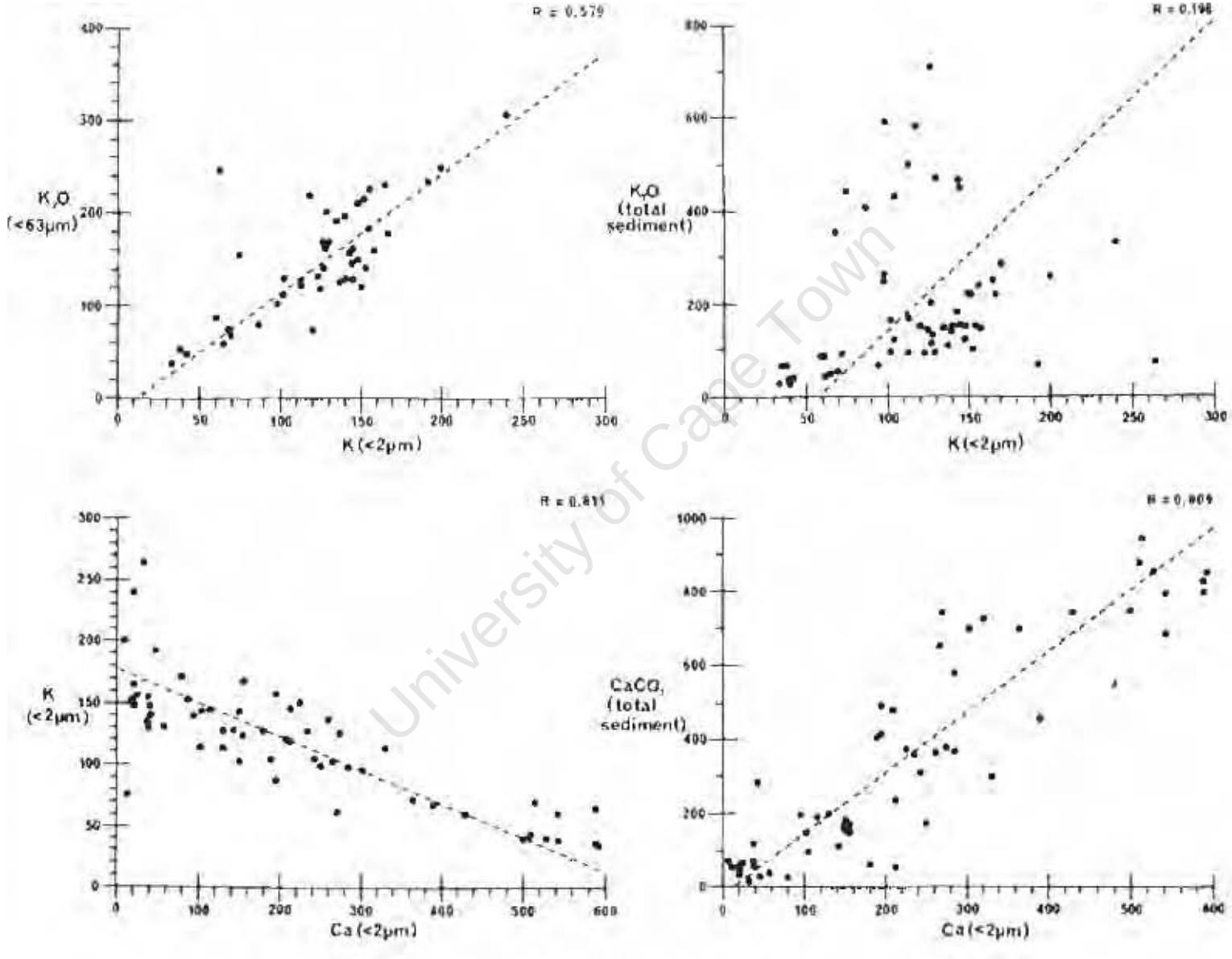


Figure III-10

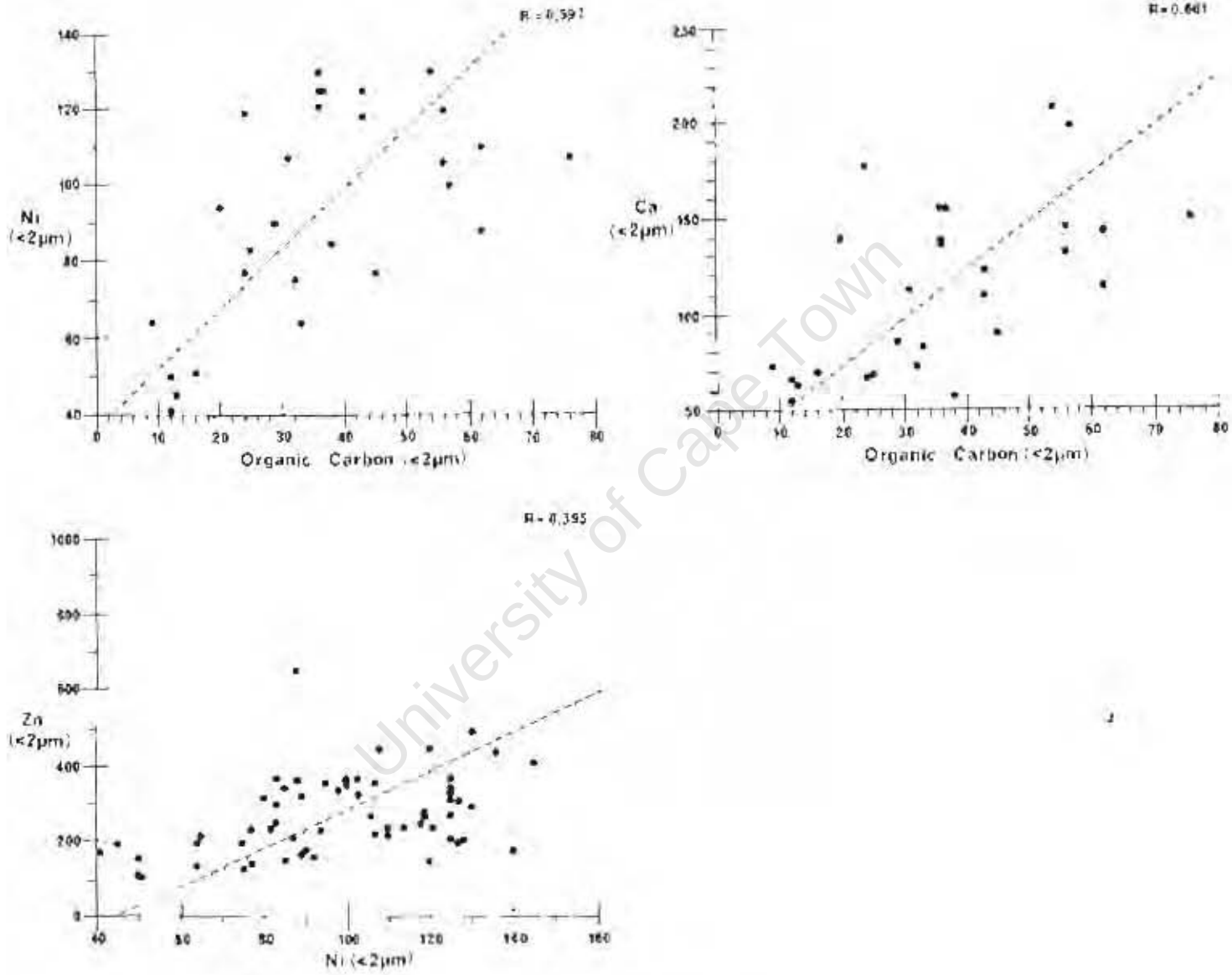
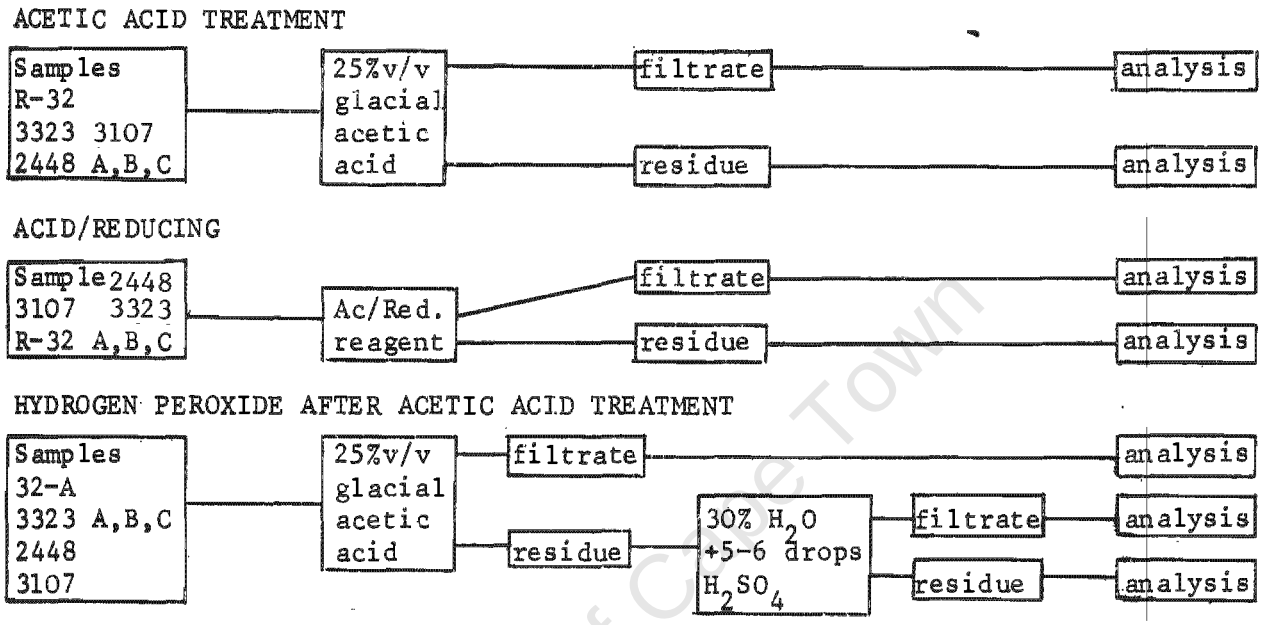


Figure III-11

reducing agent (Chester and Hughes, 1967), as well as with hydrogen peroxide in an attempt to isolate those elements related to the carbonate, surface oxide and organic phases. These samples are located in a transect across the shelf west of the Olifants River and their relationship to other geochemical and sedimentological parameters can be seen in Figure III-12. Replicates of one sample per treatment were made to determine reproducibility. The analytical procedures are described in Appendix III and are also presented diagramatically below.



(a) Glacial acetic acid treatment (25% v/v).

Minor Fe, Zn and Ni (<10%), but almost half the Mn is liberated from the river clays when treated with glacial acetic acid (Fig.III-13). Increasing amounts of Ni, Mn (up to $\pm$25%) and Zn are removed from the marine clays as they become more calcareous, whereas the quantity of Fe liberated decreases as the clays become less organic and more carbonate-rich.

The muddy nearshore sample (3323), richest in organic matter, liberated the least amounts (<10%) of all elements analysed when treated with glacial acetic acid.

(b) Acid/Reducing treatment.

Broadly similar trends as above are observed when the clays are treated with the acid/reducing agent, but a greater percentage of the total element concentration is removed.

A quarter of the Ni and over 80% of the Mn in the river clays are liberated when treated with the acid/reducing agent. As in the acetic acid treatment much less Ni and Mn are removed from the highly organic nearshore clay (3323) than from the river sample and, in a similar way to the acetic acid treatment, the percentage of the elements removed increases as the clay becomes more calcareous and less organic-rich. More Fe is released from the

organic nearshore sample than from the river clay, but again the percentage Fe liberated decreases as the carbonate component increases and the organic fraction decreases.

(c) Hydrogen peroxide treatment.

As a slightly acid solution is required for the peroxide treatment (Gad and Le Riche, 1966) the carbonate had first to be removed so as not to superimpose the effects of an acid and an oxidizing reagent. It would therefore have been convenient to use the residues from the previous acetic acid experiment for the hydrogen peroxide treatment, but as these were also analysed new samples had to be acid-treated. Results obtained during the second glacial acetic acid treatment were very similar to those described in section (a).

A far greater proportion of Ni and Zn but only slightly more Fe and Mn was liberated by the oxidizing reagent compared to the acetic acid and acid/reducing treatment (Fig.III-13). It is interesting to note that the organic-rich nearshore mud again liberated only a relatively small proportion of elements compared to the other samples.

These results will be discussed in greater detail in the following section.

3.3.6. Discussion

The geochemistry of the <2μm fraction is governed by a number of factors, the most important of which are: (i) the composition and abundance of minerals in the sample, (ii) the paths and mechanisms by which the elements are incorporated into the sediment, and (iii) the overall sedimentation pattern on the shelf (Riley and Chester, 1971). A general account of the abundance and distribution of some elements in the <2μm material was presented in section 3.3.3. and sedimentation has been discussed in Chapter II. This section will deal mainly with the paths and mechanisms whereby the elements are incorporated into the sediment.

Elements are introduced into the marine environment either in solution or associated with solid or colloidal material. In the latter group must be included elements incorporated in crystal lattices as well as those held on surfaces and in intersheet positions, ie. detrital and non-detrital fractions. The elements held in the crystal structure are derived from the continent whereas the latter can be acquired from both the terrestrial and the marine environments. In the region presently being studied, the supply of elements from non-fluviatile sources, such as volcanism and submarine weathering, are considered unimportant. Elements are incorporated in the marine sediment either directly in the solid phase or are removed from the sea water by hydrogenous or biogenous processes (Riley and Chester, 1971). Elements can be incorporated into the skeletal (Ca, Si), or soft body parts, as well as being

SOME GEOCHEMICAL PARAMETRES ACROSS THE SHELF
WEST OF THE OLIFANTS RIVER MOUTH

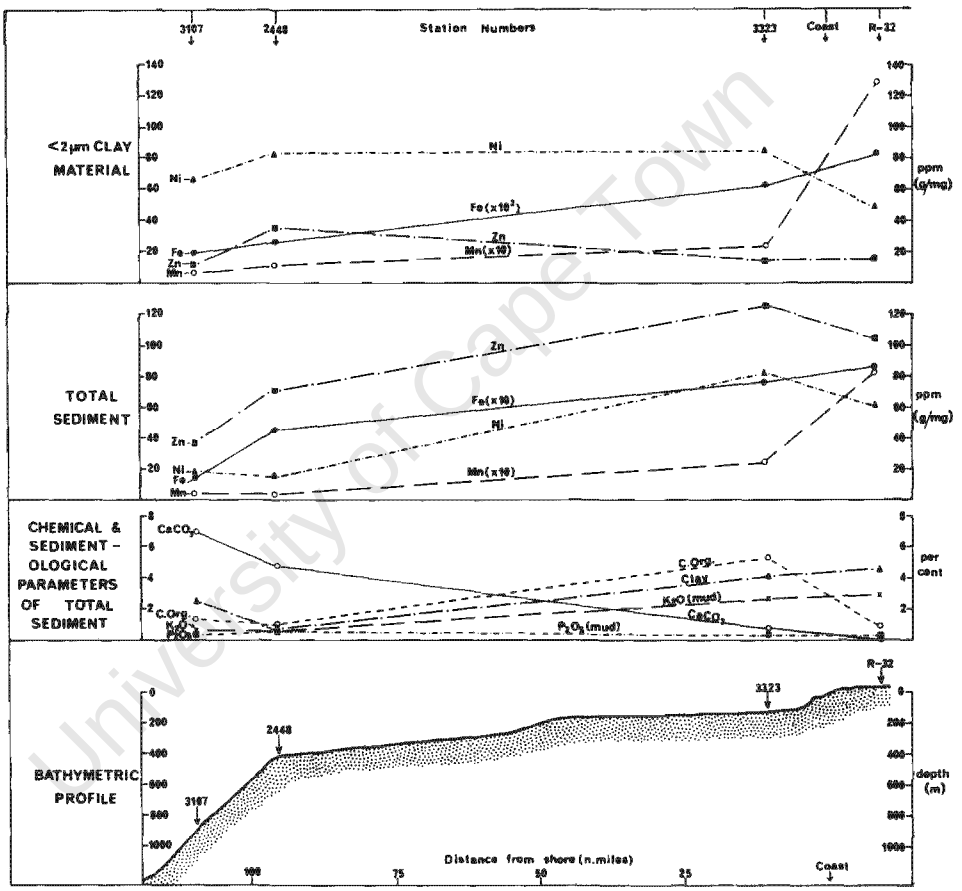


Figure III-12

THE PROPORTION OF TRACE ELEMENTS LIBERATED BY VARIOUS CHEMICAL TREATMENTS

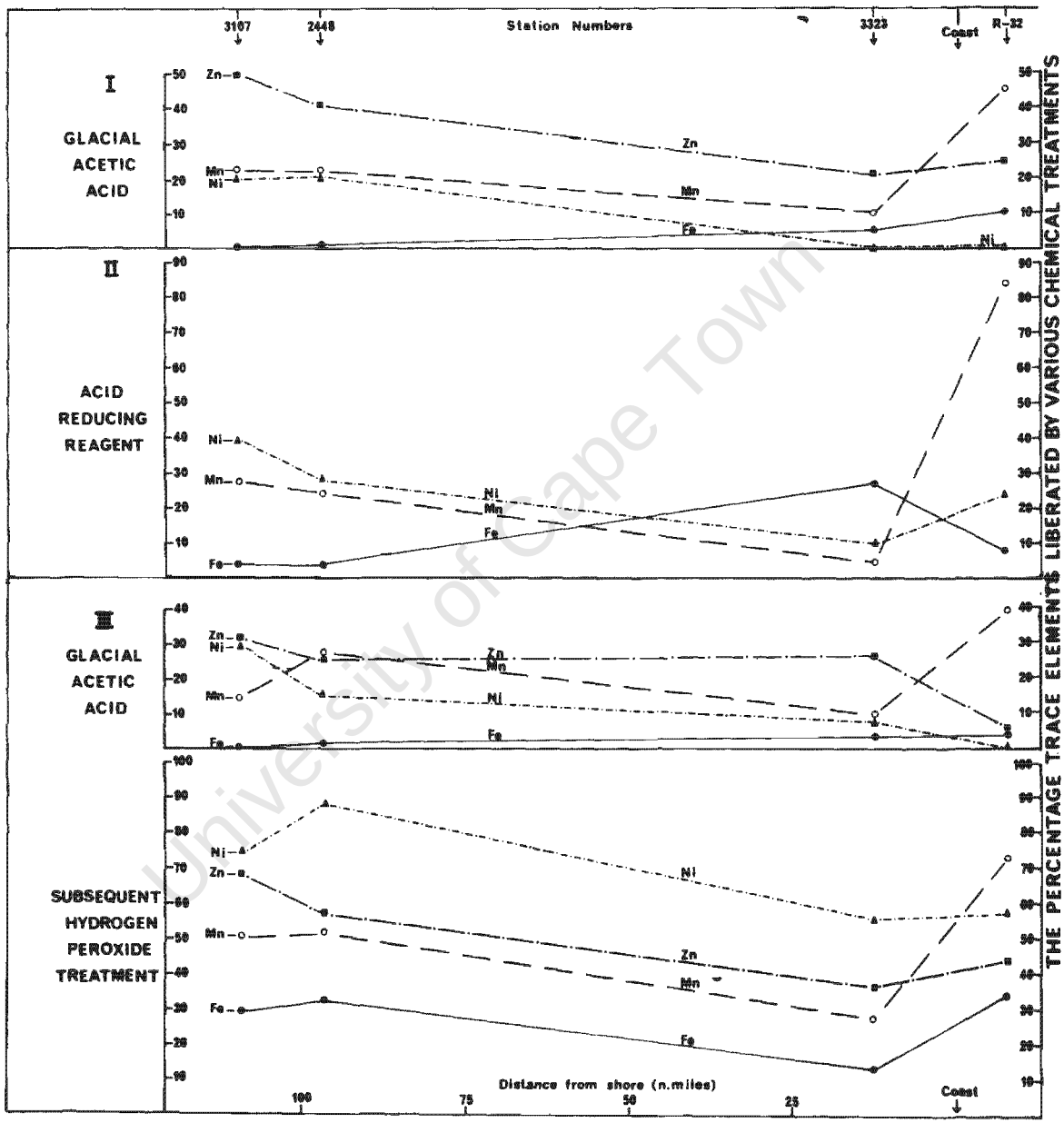


Figure III-13

associated with the bodily functions (Cu). Adsorption, co-precipitation and ion-exchange are the most important hydrogenous processes by which elements are incorporated into marine sediments.

For convenience, the elements being discussed are grouped according to their tendency to be concentrated in specific sedimentary fractions (Kieth and Degens, 1959). (a) Lattice-bound elements in clay minerals (Al, K); (b) oxidates (Fe, Mn); (c) and those elements associated with the organic and/or sulphide phases (Ni, Zn and Pb).

(a) Al and K.

The abundance of Al and K is highest in the rivers, whilst in the marine environment their concentrations decrease rapidly seawards. Despite the fact that this distribution pattern suggests strong primary terrestrial control, the importance of carbonate dilution, especially in the north, should not be overlooked. An important point when comparing marine data with other parameters is that average marine values will be suppressed owing to the presence of carbonate and therefore the non-calcareous nearshore mud values should be used when comparing the element abundances of onshore and off-shore sediments.

Al is located mainly in alumino-silicates (Gad et al., 1969) and for this reason it is commonly used as an index of the argillaceous fraction of the sediment (Goldberg and Arrhenius, 1958; Hirst, 1962(a) and El Wakeel and Riley, 1961). The average marine sediment and even the nearshore muds are impoverished in Al in relation to the onland Ecca shales (Table III-1). This may be due to the presence of considerable illite and/or substitution of Al^{++} for Fe^{++} (Nichols and Loring, 1962 and Hirst, 1962(a)).

A close relationship exists between Al and K and, like the Al, most of the K is believed to be in the alumino-silicates (Goldberg and Arrhenius, 1958 and Gad et al., 1969). Illite is known to provide a fixation site for K (Chester, 1965) and the pore water of sediments is often found to be greatly enriched in both Al (up to 100 times) and K (Goldberg and Arrhenius 1958). The average K content of the clays off the Cape coast and even the nearshore muds are impoverished in relation to the adjacent shales. This may be partly due to low determinations produced by the analytical method (see Appendix on precision and accuracy) or due to slight degradation of the clays and K desorption in the marine environment.

(b) Fe and Mn.

According to Carrol (1958), Fe may be associated with the clay mineral as an essential component; as a minor constituent in the crystal lattice; and as a surface oxide. Besides the Al/Fe substitution already mentioned, Fe can be derived directly from sea water (Goldberg, 1954) or indirectly by biological processes (Revelle, 1964; El Wakeel and Riley, 1961 and Bowen, 1966, who quotes up to 3 500 ppm dry weight for some organisms).

Negligible Fe was liberated from the clays by glacial acetic acid treatment, thereby discounting any significant Fe contribution by the carbonate phase. Only approximately 10% and 30% of the total Fe was liberated from the river clay by acid/reducing and hydrogen peroxide treatments respectively and considerably smaller proportions of Fe were released from the shelf samples by the same treatments. This is in contrast to the findings of Gibbs (1973) who has shown that approximately 40% of Fe is carried as metallic coatings and that a further 45% of Fe is incorporated in the crystal lattice. Even the most organic-rich sample from directly off the Olifants River mouth only liberated 30% of the total Fe by both the acid/reducing and the hydrogen peroxide reactions. These data suggest that most of the Fe is detrital in nature (ie. lattice bound), either as an essential constituent or as a substitution component (cf. Hirst, 1962(a)). Slight Fe enrichment in the nearshore clays in relation to the river <2μm material could be due to substitution or minor biological enhancement.

A small proportion of Mn is thought to be bound in the clay mineral lattice (Goldberg and Arrhenius, 1958) at the site of weathering, but Mn is more often co-precipitated with Fe (Hirst, 1962(a) and El Wakeel and Riley, 1961). The association of hydrated Fe and Mn oxide fractions has been explained by adsorption and by the fact that colloidal hydrous Mn oxide is negatively charged and consequently has an affinity for attracting cations, whereas Fe oxide colloids are positively charged and have a tendency for anoins (Goldberg, 1954). Biological processes have been suggested for Mn concentrations (Goldberg and Arrhenuis, 1958 and Gad et al., 1969) and high Mn values have been found in diatom samples (Bowen, 1966). Summerhayes (1972), working on the geochemistry of the total sediment from the southern part of the Cape coast found that Mn and Fe was impoverished close to the coast and that the highest values occurred on the slope and mid shelf respectively. Mn distribution was related to the foraminiferal sands and silts and the Fe to the rich deposits of glauconite.

The Mn content of the river clays is similar to that of the onland shales (Danchin, 1970) from which the river sediment is derived, but the most Mn-rich nearshore clays contain only half the average river concentration. This implies that considerable desorption takes place immedaitely the sediment enters the marine environment (Turekian, 1971). The ways in which Fe and Mn are transported are therefore considerably different. Kieth and Degens (1959) maintain that Fe forms hydrated ferric oxide and arrives in the marine environment in suspension, whereas Mn is more stable in ionic solution and therefore reaches the sea in dissolved form. More recent work (Gibbs, 1973) however, has revealed that Mn is transported mainly as metallic coatings and that incorporation into the crystal lattice and movement in solution are of

Table III-1. The chemical composition of some onland and off-shore sediments and marine plankton

ELEMENT	THIS STUDY				WORLD AVERAGES		<2µm nearshore muds	SOUTH WEST AFRICA		PHYTO PLANKTON		ADJACENT ONLAND SEDIMENTS			
	MARINE			River	shales	deep-sea calcareous sediments		min.	max.	max.	min.	Bokkeveld	Malmesbury	Ecca (western series)	Dwyka
	max.	min.	av.	av.											
	Reference				(1)	(1)		(3)	(3)	(4)	(4)	(5)	(5)	(5)	(5)
Al*	9,83	1,43	5,29	10,40	8,00	2,00	–	–	–	0,28	$7x10^{-5}$	17,60	16,90	15,80	13,80
K*	2,40	0,33	1,18	1,96	2,66	0,29	–	–	–	0,31	$3x10^{-4}$	6,20	7,50	5,60	1,00
Fe*	9,70	1,38	4,87	8,84	4,70	9,00	–	–	–	67,30	6,70	3,50	4,50	3,20	2,90
Mn	424	73	188	1101	850	1000	140 (6)	–	–	12,6	3,1	0,2	0,7	1,4	0,3
Ca*	59,20	0,80	21,81	1,01	2,21	31,24	–	18	129	45	2	19	17	24	29
Cu	295	55	141	54	45	30	26 (6) 440 (2)	3	32	47	n.d.	30	22	34	37
Pb	130	5	49	71	20	9	230 (2)	18	337	703	3	76	90	88	48
Zn	492	108	281	163	95	35	26 (6) 82 (6)	35	455	13	n.d.	37	33	25	17
Ni	145	41	99	53	68	30	29 (2)	–	–	323	2	400	700	1000	400

(1) Turekian and Wedepohl, 1961
(2) El Wakeel and Riley, 1961
(3) Calvert and Price, 1970
(4) Martin and Knauer, 1973
(5) Danchin, 1970 and Hofmeyer, 1971
(6) Parker, 1974

n.d. = not detected
* = in %, other elements in ppm (mg/g)

minor importance only. Almost 90% of the available Mn in the river clays is released by the acid/reducing reagent, almost 80% is liberated by hydrogen peroxide, and even glacial acetic acid removes 40% of the total Mn. These data indicate that the Mn is very loosely held, probably mainly as metallic coatings and associated with the organic phase.

(c) Ca.

Hirst (1962(a)) mentions four possible positions for Ca in the Gulf of Paria sediments. These are: as $CaCO_3$ in shell material; as calcium phosphate; in 12-fold co-ordination in montmorillonite; and as a component of feldspars.

The Ca-deficient source rocks supply minor Ca to the shelf as is reflected by the Ca-poor nearshore muds, but an antipathetic relationship between $CaCO_3$ and P_2O_5 indicates that little Ca is being derived from a calcium phosphate source (see also Chapter IV). The vast variation in Ca values (approx. 1% to 50%) and its relationship to calcareous organisms in the total sediment (total $CaCO_3$) is an indication of the dominant Ca contribution made by breakdown of marine flora and fauna.

(d) Ni, Zn and Pb.

Because the above elements are commonly associated with the organic matter and biogenous processes generally, the importance of these aspects of sedimentary geochemistry will now be very briefly reviewed to obviate repetition in the following discussion.

Certain trace elements can be enriched in the bottom sediment in the presence of organic matter by sorption; precipitation; formation of metallo-organic complexes; and the life processes of plants and animals (Kieth and Degens, 1959, p.49).

Sorption of ions, complexes or organic compounds may take place by reactions which are relatively insensitive to Eh, pH, and salinity, namely adsorption, absorption or cation exchange (Nichols and Loring, 1962). The principal adsorbents are clays, hydroxides and organic matter (Kieth and Degens, 1959 and Nichols, 1963). It has been found difficult to explain the distribution of elements in organic matter using atomic properties (e.g. ionic radius) alone, but it has been shown (Nichols, 1963) that elements with relative surface potentials ($^{charge}/_{area}$) of between 0,3 and 0,2 (e.g. K^+. Pb^{++}) are strongly sorbed by clays, and those in the range 0,2 to 0,25 (e.g. Zn^{++}, Mn^{++}, Fe^{++}, Ni^{++}) are sorbed by organic matter. In addition, Mason (1966) established that elements of low and high potentials (producing soluble cations and anions respectively) are readily assimilated by organic matter, whereas the intermediate elements form insoluble hydrolysates. A useful model has recently been established by Nichols (1963) to explain the incorporation of trace elements into the sediment. Organic molecules are thought to

be attracted onto the surfaces of clay particles and may constitute up to 3 or 4 times the mass of the original clay platelet. Evidence for the existence of an organic film has been gained from scanning electron microscope studies of clay particles before and after treatment with an oxidizing agent (Nichols, 1963). Organo-metallic complexes in turn show an affinity for the organic phase, hence a strong co-variance between organic matter and Cu, Ni, Mo, V, Mn etc, which readily form such organo-metallic complexes, is commonly found. Simple or aqueous inorganic ions are either unattracted by the inorganic phase ie. quartz grain or uncoated clay, or show an affinity for the clay mineral and are inhibited by the organic film formation. These elements therefore have an antipathetic relationship with organic matter (e.g. B). However, a recent investigation (Meyers and Quinn, 1974) has shown that under certain conditions organic matter can interfere with the adsorption of elements (e.g. C) normally associated with the organic phase. Obviously the role played by organic matter is not fully understood and although useful this model should be used with caution.

In regions where sea water becomes depleted of its oxygen by decaying organic matter (e.g. areas of upwelling), the metal concentration may be affected by the presence of the sulphide ion, which is capable of forming very insoluble metal sulphides and by the presence of powerful reducing agents, which may change the valence of some metals, thereby making other kinds of precipitation possible (Krauskopf, 1956). For example, trace elements (e.g. Cu, Zn, V, Pb) associated with Fe and Mn oxides can be reduced by organic matter and released, but subsequently secured by hydrogen sulphide or an organic component present in the reducing environment, (Nichols and Loring, 1962 and Wedepohl, 1964). Unlike sorption, these reactions are strongly influenced by pH, Eh, and the availability of H_2S.

Many organo-metallic compounds have been identified in sea water (Degens, 1964) and it is possible that these are as readily incorporated into the sediment as free ions. These processes are complex and poorly understood and, although important, will not be discussed in any detail here.

From the above discussion it is evident that trace element ions or complexes are stabilized in the sediment by: decrease in solubility and precipitation after reduction; precipitation as sulphides; and sorption by organic matter (Wedepohl, 1964). It is also evident that metals can be loosely classified according to their affinity for organic matter ie. heavy metals are generally "organophilic" and lighter elements are "organo-phobic" (Marchant, 1970), but that most metals show some affinity for organic matter.

It is extremely difficult to evaluate the role played by living organisms in the concentration of rare elements in marine sediment. The metal content of individual organisms varies among species; from area to area; and from one

season to another, so that average values are unattainable. Although the high metal content of some organisms has long been realized (Vinogradova and Kovalskiy, 1962; Degens, 1964 and Brongersma-Sanders, 1966), attempts are only now being made to evaluate the real contribution of the biogenous mechanism to the chemical composition of the marine sediment (Martin, 1969; Calvert and Price, 1970 and Martin and Knauer, 1973).

Phyto- and zoo-plankton are important to marine biochemistry, not only because they can concentrate vast quantities of elements, but also because they are capable of transporting them. This is accomplished by sinking skeletal detritus, moulting exoskeletons, vertical migrations across mixing barriers, movement into higher latitudes and incorporation by fast-sinking faecal pellets (Martin, 1969). Essentially two types of bio-metal can be distinguished, ie. those essential to the life processes (e.g. Mg, Fe, V, Cu) and those concentrated in proportion to the environment (Marchant, 1970). A wide literature exists (Day, 1963; Degens, 1964; Vinogradova and Grinenko, 1964; Degens, 1965; Bowen, 1966 and Monskaya and Drozdova, 1968) on the content and function of metals in organisms and some gross relative concentrations have been reported. Two examples of the degree to which some elements are concentrated in marine organisms are recorded to emphasize the importance of the biogenous processes to marine geochemistry. Calvert and Price (1970) quote the composition (ppm) of one of the most abundant diatoms off the South West African coast (Chaetoceros curvisetus) as Cu 300-6 000; Ni 60-90; Pb 1 200-1 800; Zn 6 000-9 000 and Day (1963) found that some plankton took up (ppm) Zn 2 900; Pb 6 600; and Cu 920 from water in laboratory cultures. Hogdahl (1963; in Chester, 1965) has shown that Ni is concentrated in marine organisms to a greater extent than any other element except Fe and V, and up to 2 500 times enrichment with regard to sea water has been found (Martin, 1970, see also Nichols and Loring, 1962 and Bowen, 1966).

When marine animals die and sink, bacterial attack releases trace elements to the water as organic complexes which may in turn decompose further to form ions or colloids. Dissolved and suspended organic matter may then be transported back to the surface by air bubbles present in the upper layers of the sea. On surfacing the bubble bursts and the organic matter again sinks producing an important food source for marine animals (Riley and Chester, 1971). Unconsumed aggregates adsorb trace elements from the sea water and depending on the conditions (water depth etc) may reach the sea floor. Trace element enrichment of the sea floor could take place by accumulation of the hard undissolved skeletal parts of the organism or by the elements adsorbed onto organic material. Additional enrichment could occur by concentration of faecal pellets (Martin, 1970) or even in the organism on the sea floor after death (Arrhenius, 1957; in Riley and Chester, 1971). Significant biogenous

enrichment will only occur in areas of high biological activity (e.g. regions of upwelling) where biological productivity outstrips decay.

Trace element enrichment of the bottom sediment will still not take place however, unless the metals are stabilized in the sediment. The fate of these elements in the sediment after release is poorly known (Nichols, 1963), but in an environment of organic decay, low Eh, and presence of hydrogen sulphide, it is probable that the trace element ions and complexes will be fixed by one or more of the processes mentioned above.

Ni is commonly associated with organic carbon (Fig.III-11), either sorbed directly (Nichols, 1963 and Wedepohl, 1964) or associated with clay minerals (Nichols and Loring, 1962; Hirst, 1962(b); Gad et al., 1969 and Curtis, 1969). In pelagic sediments Ni is thought to be co-precipitated by hydrous Fe oxide (Laevastu and Mellis, 1955; in Chester, 1965 and El Wakeel and Riley, 1961) or removed by the scavenging action of hydrous Mn oxide (Goldberg, 1954 and Cronon, 1970). Minor Ni may enter the clay mineral lattice at or near the site of weathering (Hirst, 1962(b) and Nichols and Loring, 1962), and in the river environment, Ni has been found to be carried equally by precipitated metallic coatings (45%) and in crystalline materials (35%) leaving only 15% associated with the organic fraction (Gibbs, 1973 and White, 1970). Ni may be removed from river immediately on entering the sea and organic-rich nearshore sediments have been found to be important areas for Ni accumulation (Turekian, 1965).

The Ni content of marine clays off the Cape west coast is enriched two to three times in relation to adjacent onshore shales and river sediment, but is impoverished with regard to the total sediment content of the diatom muds off South West Africa (Calvert and Price, 1970).

From plots of $^{Al}/_{Ni}$ against Al, Hirst (1962(b)) was able to determine the non-detrital contribution of Ni to the clay. A similar manipulation of the data from the present study produced inconclusive results, however a measure of the non-detrital phase has been gained from the partition study. Minor (<5%) Ni is liberated from the river and nearshore clays by glacial acetic acid, but as the material becomes increasingly calcareous more Ni is liberated (up to 25%). This suggests that a small proportion (<5%) of the Ni is associated with the carbonate phase (see Nichols and Loring, 1962). More Ni ($\pm$30%) is liberated by the acid/reducing treatment, indicating that co-precipitation with Fe and Mn oxides probably plays a subordinate role. Most of the Ni, however, is associated with the organic phase as indicated by the vastly increased proportion of this element released by hydrogen peroxide (Chester and Messiha-Hanna, 1970, found a similar trend in the distribution of the non-detrital fraction of Atlantic sediments).

Zn is strongly adsorbed by hydrous Fe oxide, clay minerals and organic matter (Krauskopf, 1956; Gad et al., 1969; Nichols, 1963 and Rashid, 1974). Zn is also essential to life (Bowen, 1966) and can be concentrated in marine organisms to over 5 000 times that found in sea water (Martin, 1970). The Zn content of some plankton is as high as 2 600 (Bowen, 1966) to 9 000 ppm (see Calvert and Price, 1970), most of which is concentrated by adsorption.

The Zn content of the <2µm material off the Cape west coast is more than four times that of the onland shales and river clays, but its concentration is slightly less than that of the total sediment of the diatom oozes off South West Africa. The Zn abundance reported by Summerhayes (1972) for the total sediment from the southern part of the western Cape shelf is lower than that presented here for the <2µm fraction. The Zn distribution in the total sediment, like that of the clays, shows a seaward enrichment, but the highest values occur on the slope.

Glacial acetic acid liberated between 10-25% of the Zn content of the river sample and the amount released increases (35-45%) as the sediment becomes more calcareous. The same trend applies to the hydrogen peroxide treatment, except that a far greater proportion of Zn is liberated ie. approximately 45% for the river clays and 60-70% for the outer shelf sediment. No data are available for the acid/reducing reagent owing to Zn contamination by the reagent.

Zn follows Ni in being mainly associated with organic matter, although a proportion (10-25%) of the element appears to be related to the carbonate phase or is so loosely sorbed as to be liberated by glacial acetic acid.

According to Chester (1965), Pb has two distinct mineral associations, one with clays, the other with authigenic minerals and/or biogenous debris. Although Nichols and Loring (1962) found no correlation between Pb and organic matter, this association is valid in other areas (Krauskopf, 1956; Hirst, 1962(b) and Curtis, 1969). A strong biogenous concentration mechanism is suggested by the high Pb contents in marine organisms (Nichols et al., 1959 and Vinogradova and Kovaliskiy, 1962). Pb has no bodily function (Bowen, 1966), but enrichment in marine organisms of up to 200 000 times with regard to sea water has been established (Martin, 1970).

Because of poor analytical precision no attempt has been made to assess the non-detrital Pb component of the clays and only a preliminary account of the areal distribution of Pb has been presented.

The average Pb content of marine clays from the Cape west coast is higher than that of the adjacent river and source sediments, and they are also moderately enriched in relation to the total sediment from the metal-rich diatom oozes off South West Africa. However, the Pb concentration of the <2µm material off Ireland (El Wakeel and Riley, 1961) and deep sea clays generally

is considerably higher than that of the marine clays off the Cape coast.

Pb values are highest in the most calcareous outer shelf and slope clays, possibly indicating that the Pb is being concentrated by biogenous processes. Minor enrichment off the Olifants River mouth may indicate a terrestrial influx, possibly due to pollution from the highly developed fruit industry bordering the river. However, no anomalously high Pb, Zn or Ni values have been detected in rivers draining the cultivated and highly industrialized regions of the western Cape or in the nearshore sediments bordering these areas.

3.3.7. Conclusions.

Al, K, Fe and Mn are most abundant in the source rocks and in the river sediment, whereas their concentration decreases markedly seawards on the continental shelf. Al and K are most likely incorporated into the clay mineral lattice. Both elements are impoverished in the marine sediment in relation to the onland shales and illite and kaolinite clays. Al is low, possibly owing to Al^{++}/Fe^{++} substitution, and K possibly because of degradation and K desorption of illite clay. Although Fe and Mn are both enriched in the terrestrial sediments, their mode of occurrence is vastly different. It is evident from partition studies that although a small proportion of Fe is related to the organic and oxidate phases, the majority of this element is associated with the detrital fraction. The Fe content of nearshore muds is slightly higher than the onland sediments, indicating that some additional Fe is being acquired in the marine environment. Mn, on the other hand is transported mainly in the oxidate phase and it is readily desorbed immediately it enters the sea.

Ca in the <2µm fraction is produced through the breakdown of calcareous organisms and the Ca-deficient onland sediments contribute little Ca to the shelf.

If it is assumed that the adjacent onland formations are the source of the marine sediment, then it is clear that additional Ni, Zn and possibly Pb have been acquired in the marine environment. This non-detrital fraction could have been gained in a variety of ways, among which precipitation, sorption and accumulation by living organisms are probably the most important.

Terrestrial influx onto the continental margin off the Cape west coast is moderately low (see Chapter II), whereas nutrient-rich upwelled water is locally very productive. Biogenous processes can therefore be expected to play an important role in the accumulation of certain elements. Brongersma-sanders (1966, and 1969) proposed that plankton, enriched in metals, provided the source for elements in the Kupferschiefer shales in north Germany, and Calvert and Price (1970) found that this process was operative in the intense upwelling regions off South West Africa to the north of the area presently

being investigated. The Ni content of the <2μm clays from the Cape west coast is markedly lower than that of the total sediment from off South West Africa. This suggests that the clay from off the Cape coast is not enriched to the same level as that occurring in the most intense region of upwelling off South West Africa where biogenic precipitation is dominant, but that these elements are clearly more abundant than in sediments where terrestrial influx is the predominant sedimentary mechanism, for example, in the Gulf of Paria. From partition studies it is evident that the majority of Zn and Ni is associated with the organic and/or the sulphide phases (hydrogen peroxide detroys both phases). This non-detrital fraction is thought to have been concentrated in the sediment by biogenous processes in areas of increased upwelling and biological activity in a similar way to that proposed by Brongersma-sanders (1966 and 1969) and Calvert and Price (1970).

There are several reasons why the elements (Ni and Zn) which have been enriched by biogenous processes are more abundant towards the mid shelf than in the highly organic sediments closer to the coast. Undoubtedly the most important is dilution by the high terrigenous deposition close to the coast. However, a similar off-shore increase in Pb, Ni and Zn was found by Tourtelot (1964) to be due to terrigenous organic matter contributing little to the minor element content of the sediment, whereas organic matter of marine origin played the dominant role in their concentration. The partition techniques used in this study are crude, and the importance of the various organic phases cannot be resolved. More detailed investigations of metallo-organic complexes and of incorporation of trace elements in specific organic complexes of marine and non-marine origin would be fruitful. A further contributing factor may be that while absorbing trace elements from the sea water the organisms are moved seawards by the off-shore winds which prevail during conditions of upwelling. Subsequent sinking and decay would enrich the seawater, and bottom sediments in elements seawards of the area of maximum upwelling and biological activity. Orren (1969), studying the chemistry of sea water off the Olifants River, found that Cu was most abundant in the water column between 30-50 km off shore, which tends to support the latter suggestion.

The extensive Karoo and Nama shales, coupled with high precipitation and erosion in the mountainous catchment area of the Olifants and Berg Rivers, have resulted in increased terrestrial deposition and higher Al, K, Fe and Mn values in the marine clays north of Saldanha Bay. Changes in the climate and geology in the source area have had no other detectable effects on dispersal and provenance of the fine fraction on the shelf (cf. Summerhayes, 1970), whereas the low K and P_2O_5 content of the fine fraction in the relict authigenic regime tends to discount any possibility of present-day glauconite or phosphorite formation.

CHAPTER IV. THE GLAUCONITE AND PHOSPHORITE DEPOSITS

4.1. Introduction

One of the most extensive glauconite and phosphorite deposits in the world occurs off the south and west coasts of southern Africa. Large areas of the Agulhas Bank and the west coast as far north as the Kunene River are covered by phosphatic sediment. These deposits have been formed by replacement of previously existing calcareous debris, mainly lime mud, on the sea floor. In contrast, more restricted quartzitic phosphorites found onshore formed contemporaneously by precipitation. The latter are analogous to the rich pelletal phosphorite deposits off South West Africa which are thought to be forming at the present time. Both phosphorite types are related to upwelling of nutrient-rich Atlantic Central waters, but environmental differences have dictated different diagenetic mechanisms for their formation.

Extremely rich glauconite deposits occur on the Agulhas Bank and on the shelf off the west coast of southern Africa. Although their distribution is also related to regions of upwelling, their occurrence tends to be more localized.

An association of glauconite and apatite has frequently been reported in marine sediments, but integrated studies of these two minerals are rare (Summerhayes, 1970). The present investigation has revealed that glauconite and apatite are often intimately associated and this complex relationship has been studied on a macro-(total sediment geochemistry) and microscale (microprobe analyses of individual mineral phases).

The nature and the distribution of glauconite and apatite as well as the inter-relationship between these two phases are discussed in this chapter.

Because the phosphatic material described in the following pages has been formed by replacement and precipitation mechanisms the following genetic classification has been adopted in this work:

Phosphorite and collophane: Rocks on the continental margin which have been formed by replacement of calcareous material. They contain a heterogeneous mixture of quartz, glauconite, calcite and collophane cement. Strictly, the term phosphorite is reserved for sedimentary rock containing over 18% P_2O_5 (equivalent to 50% apatite), but in this work it will be used in a colloquial sense to denote any lithified rock containing >5% P_2O_5 (cf. Parker, 1971 and Siesser, 1971). Collophane is used as a 'sack' name for a number of cryptocrystalline marine apatites. Deer et al. (1962) regard dallhite as an apatite containing 'abundant CO_2' but minor F and francolite has an 'appreciable' CO_2 content and >1% F. The chemical formula proposed by

Altschuler et al. (1958) for the carbonate-fluorapatite found in phosphorites is $Ca_{10}(PO_4, CO_3)_6F_{2-3}$.

Quartzitic phosphorite: Rocks composed of quartz cemented by collophane and are considered to have been formed by precipitation. Found mainly onland in the vicinity of Saldanha Bay, but one sample has been recovered from the continental shelf.

Pelletal phosphorite: Medium sand-size pellets formed by reworking of quartzitic phosphorite. They are abundant off South West Africa and onshore in the vicinity of Saldanha Bay, but only small amounts occur off the Cape west coast.

Cement: Refers to intergranular collophane, micrite, goethite and glauconite which cement the silt, sand, and pebbles together.

Matrix: Applies to conglomerates, and refers to all material except pebbles.

Mature glauconite: Black or dark green pellets which form the end members of the glauconitization process, containing no expandable material, having more than 8% K_2O, and correlating with the "ordered" glauconite defined by Burst (1958(a)). The general formula given by McRae (1973) for glauconite is $K_{0.76}(Na,Ca)_{0.13}(Al_{0.40}Fe_{0.87}^{3+}Fe_{0.49}^{2+}Mg_{0.40})Si_{3.42}Al_{0.58})O_{10}(OH)_2$.

Immature glauconite: Glauconite which has not undergone complete diagenesis and contains expandable clay minerals and less than 8% K_2O.

In this investigation, especially in the microprobe studies, it was not always possible to identify the mineral species present, and therefore some non-specific terms, including 'collophane', 'apatite' and 'phosphatic material', have been used to describe Ca-P-rich minerals. X-ray diffraction and bulk geochemical studies indicate that the primary phosphate mineral present is francolite.

4.2. Methods

X-ray diffraction studies were made on a Philips (PW 1050/30) goniometer fitted with a sealed proportional detector using Ni-filtered Cu K α radiation. Powdered (less than 250 mesh) phosphorite was pressed into briquettes which were scanned (1) from 4 to 60°2θ at 2°2θ/ minute to assess the general mineralogy of the rock, and (2) from 51.5 to 53°2θ at ½°2θ/ minute to calculate the CO_2 content of the apatite phase using a peak-pair method described by Gulbrandsen (1970). Instrument settings were the same as those used in the clay mineralogy study.

Most of the major elements (Si, Ti, Al, Fe, Mg, Ca, K, Na, P and Mn) were determined by X-ray fluorescence spectrometry, using methods adapted from Norrish and Hutton (1969); F and organic carbon were analysed by wet chemical methods. Loss on fusion was determined by weight loss on heating the sample to 1000°C.

The electron-beam scanning and micro-analytical facilities of the Cambridge Microscan V microprobe were used to study the composition and dispersion of individual mineral phases. Elements determined were Si, Al, Fe, Mg, Ca, K, Na, and P. S was included in some analyses of phosphatic material thought to have formed under strongly reducing conditions.

Results of the bulk and microprobe analyses as well as a description of the methods employed, are summarized in Appendix IV.

4.3. Glauconite from the continental margin

4.3.1. Introduction.

Obtaining reliable chemical data on glauconite is an extremely difficult task (Burst, 1958(b); Bentor and Kastner, 1965 and Birch and Willis, 1974) not only because every contaminated, oxidized and altered grain must be extracted from a bulk sample by hand, but also because many grains are composite and contain impurities in the form of other mineral phases. It is often impossible to hand pick samples as impurities are sometimes only discernible in thin section or by X-ray analyses. In spite of these difficulties, previous geochemical studies made by Birch (1971) showed that South African glauconites manifested chemical and mineralogical trends controlled by diagenic processes.

In order to acquire reliable chemical data on uncontaminated, unaltered pellets and to trace the chemistry of the glauconitization process the present electron-microprobe investigation was undertaken. Only two other microprobe investigations (5 analyses) have been made on glauconitic material. A single analysis of a "glauconie", foraminiferal infilling was reported by Bjerkli and Østmo-Saeter (1973), and Burnett (1974) has presented four analyses of glauconite from the Peruvian-Chilean shelf. Birch and Willis (1974) have presented microprobe analyses of glauconites and phosphorites in an earlier interpretation of the data presently being discussed.

Mineralogical data were taken from Birch (1971) because to acquire structural data compatible with the microprobe determinations would necessitate special techniques involving single grain analyses.

4.3.2. Microprobe investigations of glauconite grains.

As the composition of glauconite is variable, and because no comparative data exists, it was first necessary to carry out repeated analyses of one glauconite type from a few locations to establish the degree of intragrain homo-

geneity and to determine the precision of the analytical method. Replicate analyses were made on 10 mature glauconite pellets from the two main glauconite deposits, and on a further 10 mature glauconite pellets from other locations on the shelf. A further 27 pellets at different stages of maturity, were analysed in an effort to elucidate the chemical changes which take place on glauconitization. The glauconite grains were grouped into four stages of maturity (Plate IV-1) based on the following petrographic criteria(listed in order of increasing maturity):-

1st stage: Light yellow- or brownish-green, slightly sutured with an irregular outline, and with common inclusions of silt-sized quartz or shell fragments (Plates IV-2 and 22).

2nd stage: Yellow-green, sutured, with a subrounded outline, and with no inclusions.

3rd stage: Uniform gray-green, very sutured, with rounded outline.

4th stage: Unifrom dark green, non-sutured to slightly sutured, and generally well rounded.

Supplementary studies were made of oxidized grains and glauconites showing strong zoning to determine how the observed colour variations were related to chemical composition.

(a) The mineral glauconite.

The maximum theoretical K_2O content for glauconites has been calculated at 8,7%, but for Al 2:1 contracted layer minerals it can be as high as 9,9% K_2O (Cimbálinková, 1971; from Weaver and Pollard, 1973). Generally, glauconite containing more than 8% K_2O or even possibly greater than 7% K_2O is considered to be pure "mature glauconite" (Burst, 1958(b) and McRae, 1972). The most mature glauconites (4th stage) from off the Cape west coast all contain over 8% K_2O (Table IV-1), have a maximum content of 9,47% K_2O and a mean value of 9,01%, so can be considered to be pure.

Judging from the literature, this K_2O content seems high, probably because the analyses reported are bulk determinations which will include some non-glauconitic material.

Glauconite analyses are generally contaminated by non-structural Fe or are affected by the inclusion of oxidized grains. It is therefore interesting to note the large range in Fe_2O_3 values (16,6 to 23,04% Fe_2O_3) that occurs in this group of analyses, and also that the average bulk determinations for the Agulhas Bank glauconites are similar to the more recent probe data, ie. 21,22 and 21,01% Fe_2O_3 respectively. Apparently non-structural Fe and oxidized grains are not important in glauconites from this region.

The variation in the SiO_2 content (47,7 to 52,2%) is not as much as that reported by most workers (Bentor and Kastner, 1965 and Hutton and Steelye, 1941), and the Al content ranges markedly (1,77% to 7,01%). Such a variation

is common because Al can substitute for Fe in the glauconite structure (McRae, 1972 and Weaver and Pollard, 1973). The low Na_2O (0,07%), CaO (0,18%) and P_2O_5 (0,15%) content indicate that the mineral is free of apatite.

Glauconites from the Cape have a greater range in Mg values (3,75 and 6,23%) than is normal for glauconites and the average value (5,45%) is high in relation to glauconite reported in the literature (4%, McRae, 1972).

(b) Immature glauconite and the glauconitization process.

Glauconites containing <8% K_2O have been grouped into 3 classes according to maturity (Appendix IV). The range in elemental abundance for all the glauconite analyses appears below, and the mean values for some of the elements in each group are presented in the form of a variation diagram (Fig.IV-1).

	SiO_2	Al_2O_3	Fe_2O_3	K_2O	MgO	Na_2O	CaO	P_2O_5
Maximum	52,22	7,39	27,27	9,47	6,23	0,57	3,51	0,58
Minimum	43,22	1,97	16,62	4,64	3,75	0,02	0,04	0,03

McRae (1972) has combined the various glauconitization theories (excluding precipitation) into two groups:- the "layer lattice theory" (Burst, 1958(a) and (b) and Hower, 1961) and the "epigenetic substitution theory" (Ehlmann et al., 1963; Seed, 1968 and others). According to Burst's model, the formation of glauconite simply requires any degraded 2:1 layer lattice structure with a low lattice charge as a parent material. The glauconitization process involves a gradual substitution of Fe for Al in the octahedral position, resulting in an increase in octahedral lattice charge and a consequent increase in "charge-balancing" interlayer cations (mainly K). This causes the collapse of increasingly more expandable layers to a 10Å non-expandable type.

The alternative theory was initially proposed to explain the preferential replacement of calcite by glauconite (McRae, 1972), but has been used to explain the replacement of many non-micaceous silicates, e.g. quartz, feldspars, pyroxenes, olivines etc. (Ojakangas and Keller, 1964 and Dapples, 1967).

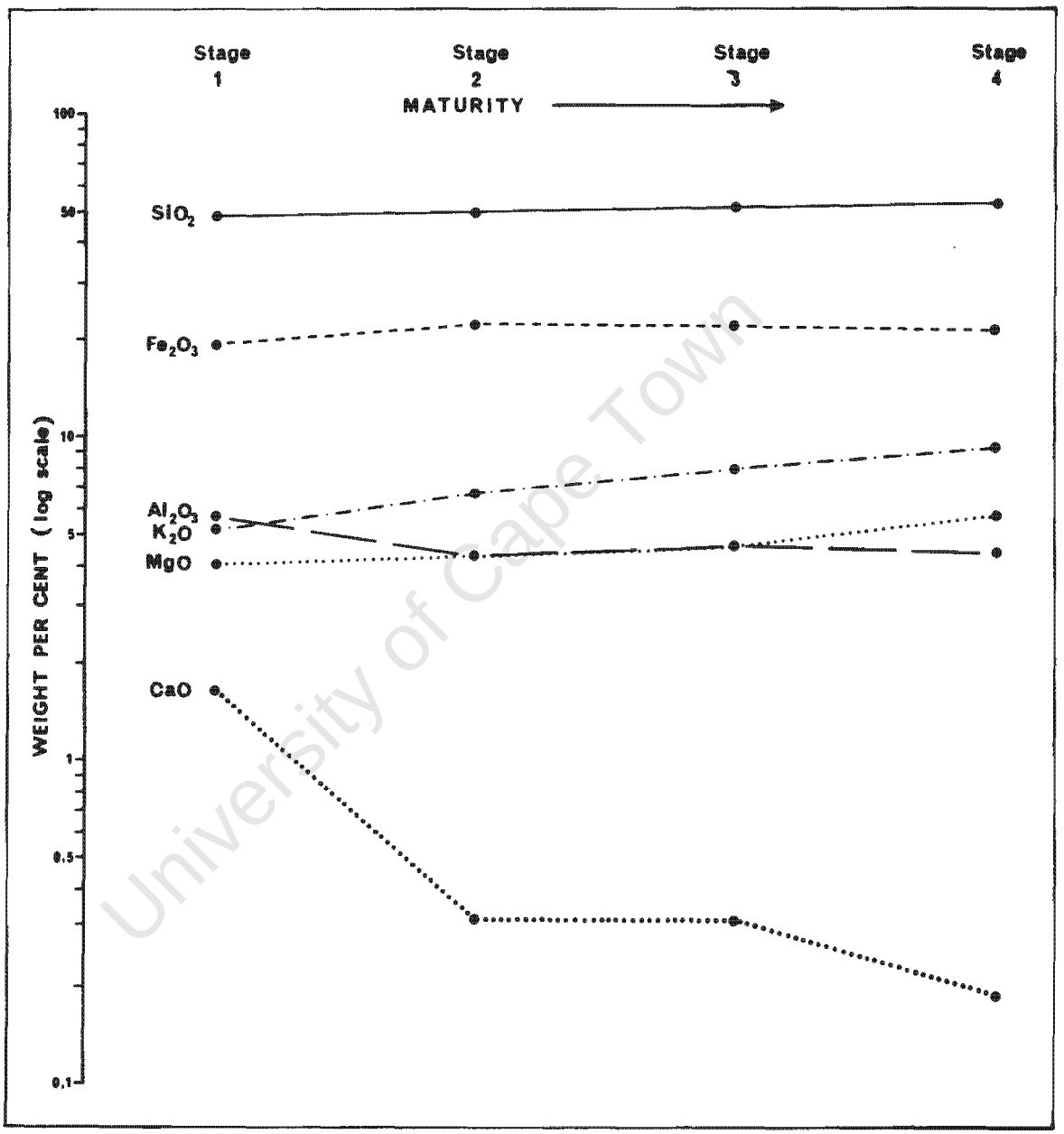
Although there is ample evidence for both theories, there is general agreement that most glauconites are formed by alteration of micaceous material. Nevertheless, the precise mechanism involved in the diagenetic change is still obscure. There is clearly disagreement with regard to the roles played by Fe and Mg in the glauconitization process. The model proposed by Burst (1958 (a) and (b)) and Hower (1961) predicts that the increase in net lattice charge is caused by substitution in the octahedral layers. The number of interlayer cations (mostly K) would increase with the net octahedral charge and therefore there should be no relationship between the abundance of interlayer cations and the tetrahedral charge.

Table IV-1. Average composition of glauconitic material as determined by microprobe analysis.

	Glauconite pellets					Foraminiferal infillings	Altered faecal pellets
	1st stage	2nd stage	3rd stage	4th stage	oxidized		
No. of analyses	6	12	9	20	5	3	1
SiO_2	48,03	49,39	50,81	50,97	28,08	47,76	54,15
Al_2O_3	5,74	4,30	4,56	4,29	4,00	6,42	5,92
Fe_2O_3	19,14	22,43	21,86	21,01	44,73	19,53	19,15
MgO	4,04	4,25	4,46	5,45	2,83	4,72	4,91
CaO	1,68	0,32	0,32	0,18	0,30	2,15	0,48
Na_2O	0,14	0,19	0,08	0,07	0,11	0,06	0,12
K_2O	5,22	6,73	7,96	9,01	3,40	6,92	8,56
P_2O_5	0,19	0,20	0,17	0,15	0,52	0,39	0,25
Total (1)	84,18	87,81	90,22	91,13	83,97	87,95	93,54

(1) Low totals are due to the water content which varies from up to 16% for immature glauconites to 8% for the most mature types (Birch, 1971).

VARIATION DIAGRAM ARRANGED IN GROUPS ACCORDING TO MATURITY OF GLAUCONITIC MATERIAL



The following trends are observed:-

(1) SiO_2 and MgO increase with increasing K_2O

(2) CaO and Al_2O_3 decrease with increasing K_2O

(3) Fe_2O_3 displays no consistent trend with increasing K_2O

These trends are confirmed in the scatter diagrams of individual analyses (Figs.IV-2 and 3)

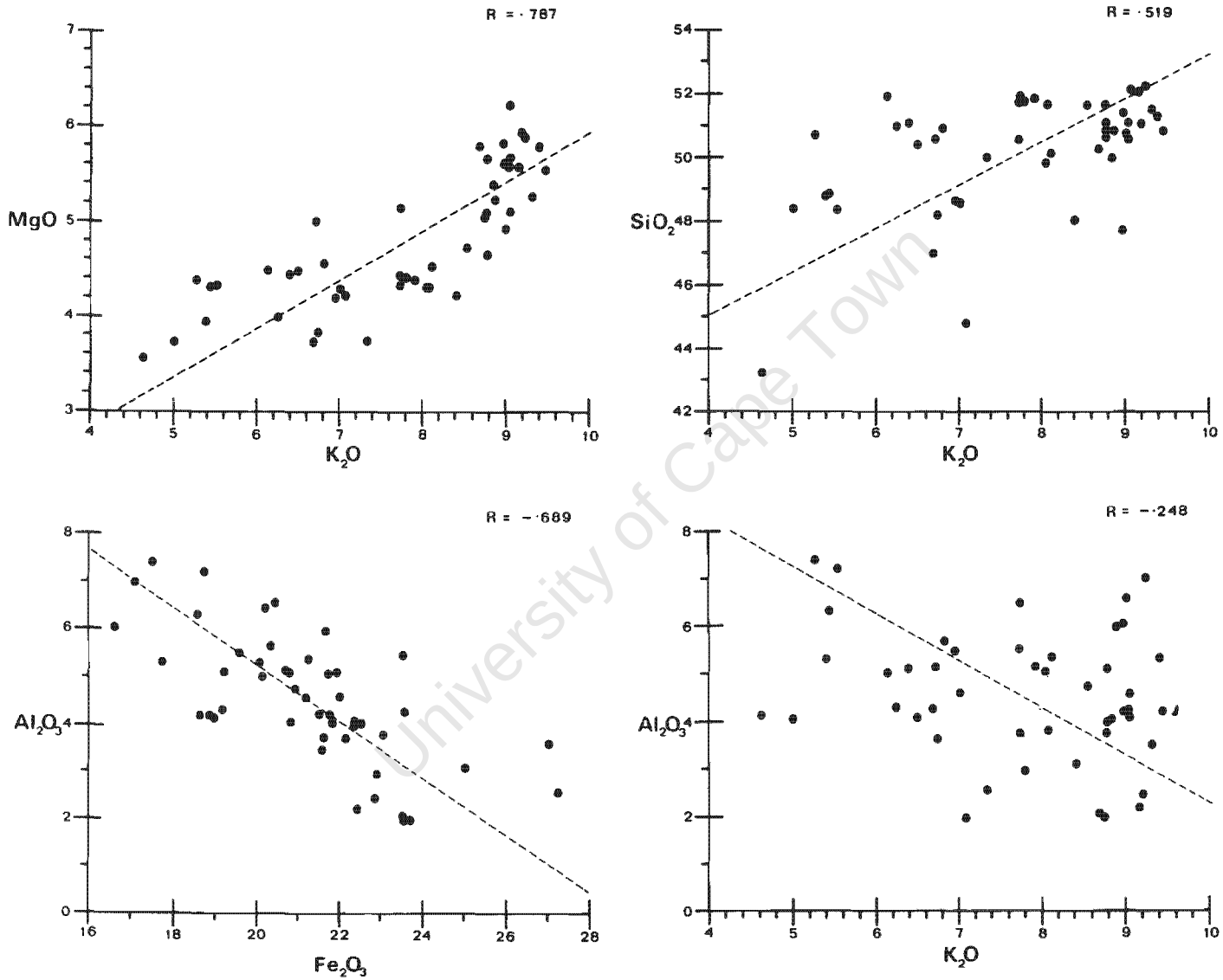
Figure IV-1

If this model is correct, K and Fe should be proportional to each other and inversely proportional to the number of expandable layers. However, several recent studies (Bentor and Kastner, 1965; Foster, 1969 and Weaver and Pollard, 1973) have found no such relationship and data obtained in the present investigation seem to substantiate that no relationship exists between K and Fe. An alternative theory considers the process of glauconitization to be of "two separate unrelated processes; incorporation of Fe into the crystal structure and fixation of K in interlayer positions with the incorporation of Fe and development of a negative layer charge preceding the complete fixation of K". (Foster, 1969, p.F14).

Hower (1961, p.326) considers the Fe and K to be "adsorbed" contemporaneously from the sea water onto a degraded layer, but there is no evidence in the present data to suggest that this relationship exists (Fig.IV-3). This may be due to all the Fe being assigned to the ferric state which may be masking subtle relationship between K_2O and FeO or Fe_2O_3. The least potassic material determined in this study (4,6% K_2O) contained over 19% Fe_2O_3 and the glauconite with the highest K_2O content (9,4%) only contains 18,88% Fe_2O_3. These data (Figs.IV-2 and 3) tend to support Foster's theory. Similar relationships have been found by Ehlmann et al. (1963); Seed (1965); Bentor and Kastner (1965) and Foster (1969). The most immature glauconite infillings found by Ehlmann and others contained 4,31% K_2O and 22,3% Fe_2O_3, and similarly Bjerkli and Östmo-Saeter (1973) analysed a glauconie (an immature glauconite) infilling which contained only 2,77% K_2O but 18,71% FeO.

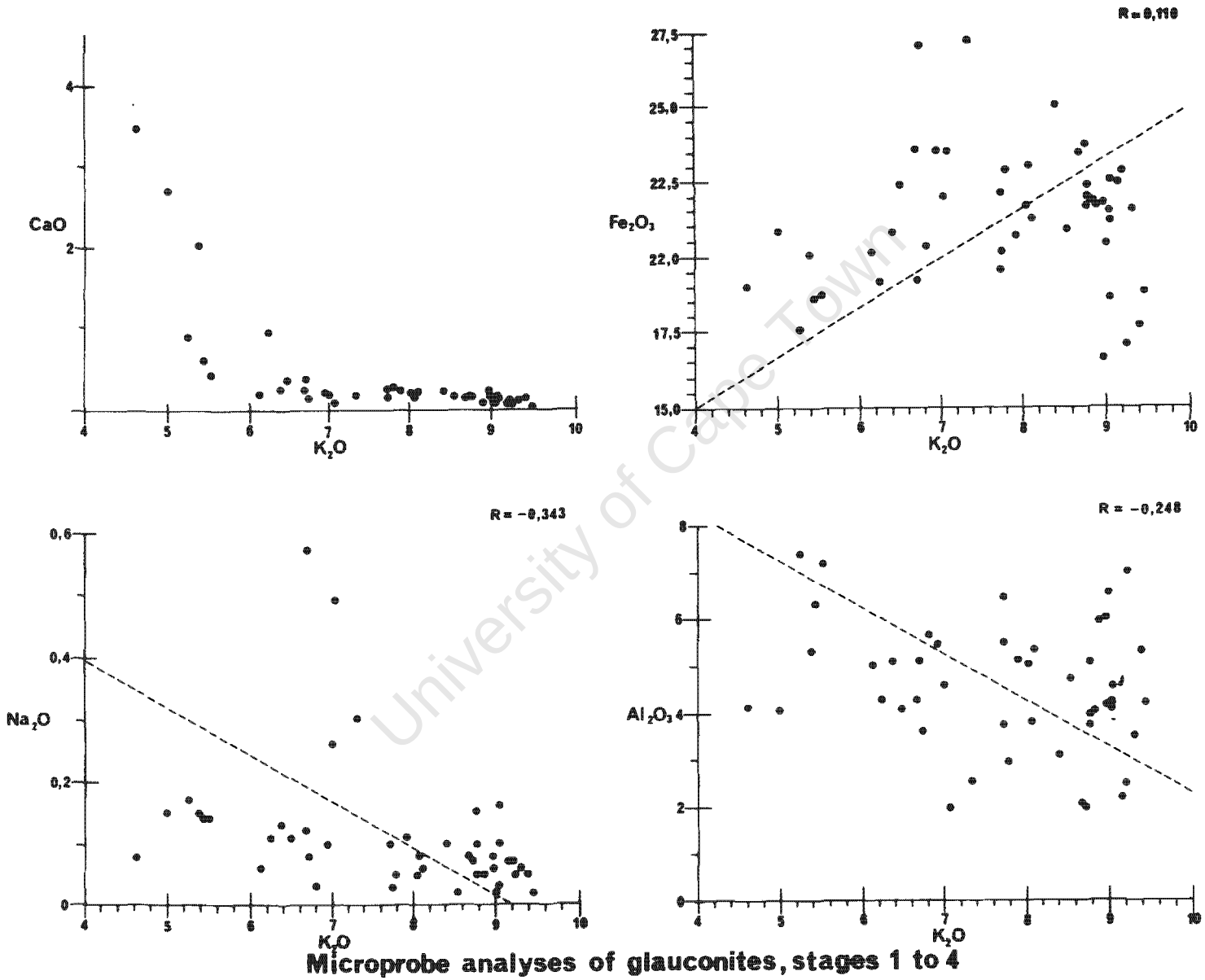
Ross and Hendricks (1945) allocated all the MgO in glauconite to the octahedral layer and obtained octahedral occupancy of as high as 2,24 positions. From this they concluded that octahedral occupancy in some dioctahedral minerals is not necessarily limited to two-thirds of the available cationic octahedral positions, but that as much as a fourth of the "vacant" third positions might actually be occupied. Bentor and Kastner (1965) also found a "excess" (between 2 and 33% of the total Mg^{++} present) of Mg, but explained it in another way. Only by assuming that some of the Mg^{++} in the octahedral layer was not replacing Al^{+++} but was adding to it, could the negative lattice charge be balanced by the amount of adsorbed K^{+} cations present. The (060) position of glauconite (1.51 to 1.53Å) is intermediate between that of a dioctahedral (1.50Å) and a trioctahedral (1.54Å) 2:1 layer clay. Warshaw (1957) and Bentor and Kastner (1965) present this as independent evidence for some trioctahedral layers being intergrown with octahedral layers.

MgO is invariably assigned completely to the octahedral layer; Al^{+++} and Fe^{+++} account for approximately 80% of the positions in the octahedral sheet, (Jung, 1954, in Millot, 1970) and Mg^{++} and Fe^{++} constitute about equal proportions of the remainder (Foster, 1951 and Weaver and Pollard, 1973).



Microprobe analyses of glauconites, stages 1 to 4

Figure IV-2



Microprobe analyses of glauconites, stages 1 to 4

Figure IV-3

Köster (1965) plotted MgO against K_2O to show that Mg in the octahedral layer was directly related to the quantity of interlayer K. Similar evidence (Foster, 1951; Owens and Minard, 1960 and others) of exchangeable interlayer MgO has led Foster (1969) to consider all Mg in excess of 2 octahedral cations as being present in the interlayer position.

The concentration of all elements would increase with increasing K_2O because of the dehydration that accompanies the glauconitization process, but the marked enrichment in MgO with increasing K_2O (Fig.IV-2) as well as the unusually high MgO values determined in this investigation would favour the supposition that some Mg is being incorporated with K in the interlayer position.

Ca and Na are usually assumed to be present as exchangeable cations firmly fixed in the interlayer position (Weaver and Pollard, 1973). The only relationship between the interlayer cations exhibited by these data is a general decrease of Na and Ca with increasing K (Fig.IV-2). This suggests that K and Mg increase in the interlayer position at the expense of Ca and Na. High Ca values in some immature glauconites (ie. up to 3,5%) are not associated with interlayer adsorption or an apatite phase (P_2O_5 values <0,13%), but are probably due to the presence of minor calcium carbonate (Plate IV-2 and 22).

To summarize, these data suggest that Fe is emplaced into the clay structure very early in the glauconitization process, possibly by a mechanism which is independent of and prior to the fixation of K. The sympathetic relationship between K_2O and MgO tends to support a recent contention that some Mg is located in the interlayer position and no substitution of Ca or Na for K is apparent.

(c) Glauconitic foraminiferal infillings and faecal pellets.

Of the 16 foraminiferal infillings analysed, only 3 were composed of uncontaminated glauconitic material, the remaining samples being phosphatic or highly ferruginous. Similarly only one of the 11 faecal pellets analysed was purely glauconitic.

These results are similar to those obtained for the glauconite grains described earlier and serve only to confirm the presence of abundant Fe as well as that of calcium carbonate in immature glauconite. It is also interesting to compare these results with those presented by Bjerkli and Ösmo-Saeter (1973) for a glauconie infilling from off the Scandanavian coast.

	SiO_2	Al_2O_3	Fe_2O_3	K_2O	MgO	Na_2O	CaO	P_2O_5
Bjerkli and Östmo-Saeter)	28,56	6,06	18,71*	3,77	2,92	tr	8,57	-
Most immature infilling determined in this study	45,21	6,14	20,15	5,92	4,21	0,05	5,07	0,35

*Bjerkli and Östmo-Saeter present total Fe as FeO.

The presence of abundant Fe and high Ca (probably as $CaCO_3$) in the most immature glauconite phase is substantiated by both studies, and the composition of the glauconitic faecal pellet is similar to that of the 4th stage glauconites.

(d) Oxidized grains.

Rim and centre analyses were made of two glauconite grains exhibiting brown oxidation rims (Plate IV-1) to determine the chemical changes which occur during the oxidation process.

STATION GiL-574

	Grain W/16		Grain S/7		Other grains			Oxidized grain from Peru (1)
	un-oxidized centre	oxidized rim	un-oxidized centre	oxidized rim	oxidized V/13	oxidized V/7	un-oxidized U/6	
SiO_2	48,13	37,14	34,16	32,66	22,29	14,22	50,00	14,84
Al_2O_3	3,60	4,24	3,94	4,35	3,75	3,73	2,55	3,13
Fe_2O_3	27.07	31,49	36,06	41,50	52,37	62,21	27,77	60,85
K_2O	6,75	5,01	3,93	4,18	2,95	0,91	7,35	1,75
MgO	3,83	3,67	3,07	2,95	2,70	1,75	3,75	2,14
CaO	0,14	0,28	0,29	0,36	0,31	0,25	0,18	0,24
Na_2O	0,57	0,05	0,13	0,17	0,20	0,00	0,30	0,56
P_2O_5	0,14	0,29	0,35	0,50	0,65	0,82	0,08	1,65

(1) Burnett, 1974.

Grains from station GiL-574:

W/16 and S/7: dark green, well-rounded glauconite grains with oxidized rims.

V/13 : very dark green, oxidized glauconite.

V/7 : large, golden-brown completely oxidized glauconite.

U/6 : large, rounded , dark green grain with unoxidized appearance.

The results show that a decrease in Si is accompanied by an increase in Al and Fe, but the abundance of the other elements remains fairly constant. Although not so obvious in the surface and centre analyses, it is apparent from the analyses of the more oxidized grains (V/13 and V/7) that under conditions of increased oxidation there is a loss in all elements other than Fe, and from other studies (De Coninck and Laruelle, 1964; in McRae, 1972) it is known that

the characteristic brown rim is at least partly due to the Fe reverting from the ferrous to the ferric state. The glauconite structure breaks down under extreme oxidation and Fe is liberated and accumulates as hydrated Fe oxide, usually referred to as limonite (McRae, 1972) or goethite (Bentor and Kastner, 1965). Other iron-rich weathering products that are mentioned in the literature are siderite, hematite, magnetite and jarosite (see McRae, 1972), but no attempt has been made to identify these phases in the present study.

(e) Zoned glauconite pellets.

Glauconite pellets from the nearshore deposit west of Hondeklip Bay are uncommonly large (>1 mm) and often exhibit poorly defined internal colour zonation (Fig.IV-4). The colour varies between dark brown-green and light lime-green and frequently follows the grain outline or sutures within the pellet. It was initially thought that this colour variation reflected a change in chemistry, perhaps a variation in the Al-Fe content or a change in the oxidation state of Fe.

To test these possibilities, X-ray images and line scans were made of two grains showing pronounced zoning. The X-ray images were incapable of resolving subtle changes in composition and therefore the grains were "mapped" by running several X-ray line scans of Si and Al across the pellets and plotting the values at regular intervals along each traverse. These values, in raw counts, were then contoured (Fig.IV-4). Results indicate only minor variations in Si, but a marked centre-to-surface increase in Al. The Al values increased, almost regularly, by a factor of two from the centre to the rim for both grains analysed. Small areas (<4μm) were also detected within the pellets which were so enriched in Al that the recorder went off the scale. The distribution in Al is clearly not related to the colour variation. However, it was observed that the counts on the line scans frequently dropped off to zero for both elements along the traverses. This is thought to be due to the presence of organic matter in the pellet, and these areas are directly related to the lighter coloured regions of the grain. It would therefore appear that the colour variation at the surface of the pellet and along the sutures within the grain is due to oxidation of organic matter by the surrounding sea water.

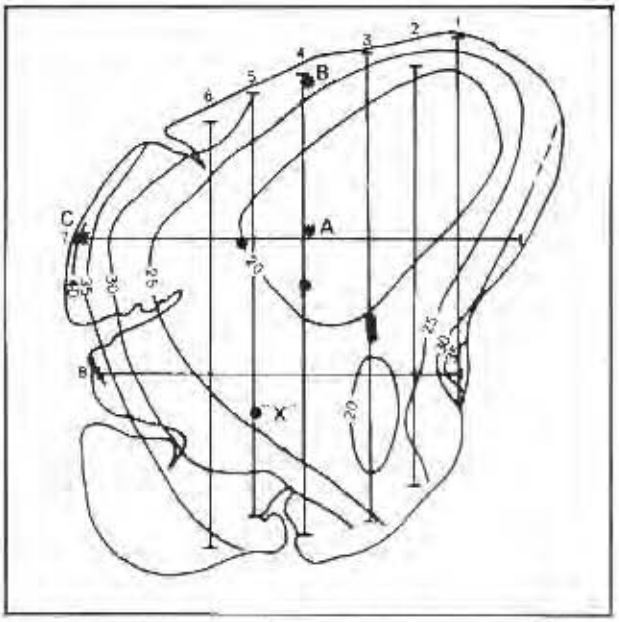
The small Al-rich areas are possibly remnants of unglauconitized clay material and the increase in Al and K towards the rim of the grain clearly indicates increased glauconitization towards the outer margin of the pellet.

4.4. The off-shore phosphorite rocks

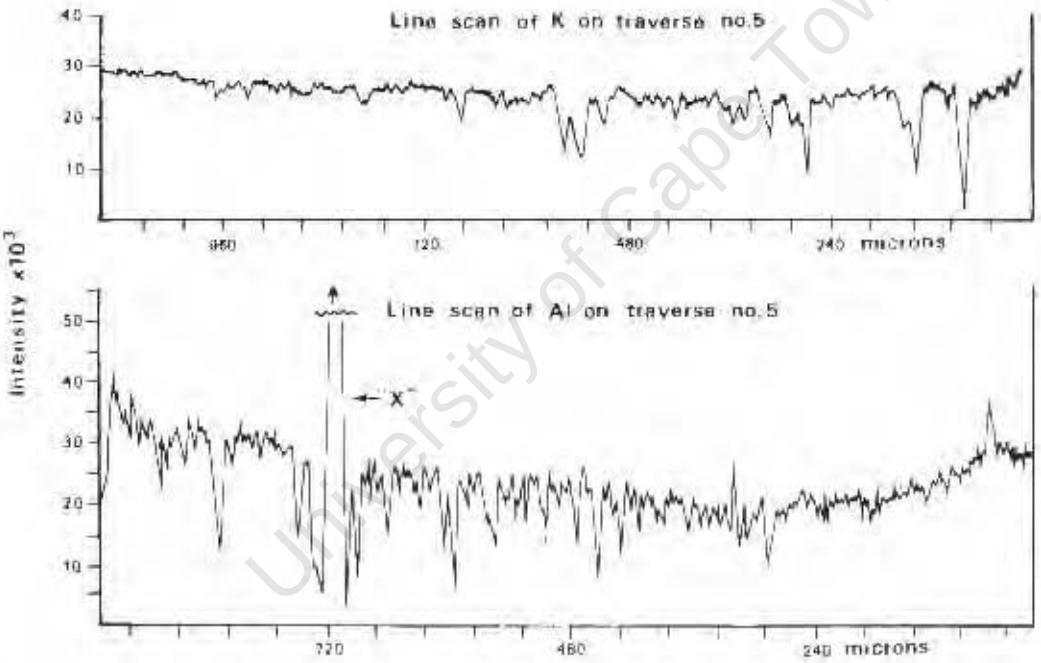
4.4.1. Introduction.

Investigations made on Agulhas Bank phosphorites since they were first recovered in 1873 by Murray and Renard (1891) have been thoroughly reviewed by

Photomicrograph



Aluminium distribution in raw counts x10^3
Dots represent isolated areas rich in Al,
see X-ray scan below



MICRO - ANALYSES

	A	B	C
SiO_2	50,15	51,32	50,15
Al_2O_3	1,49	2,37	2,62
Fe_2O_3	27,37	27,75	27,97
MgO	5 05	4,86	4,79
CaO	0,16	0 07	0,11
Na_2O	0,29	0,21	0,18
K_2O	7,98	8 48	8,67
P_2O_5	0 14	0,11	0 14
Total	92,63	95,17	94,63

Figure IV - 4

Parker (1971) and Dingle (in press).

Early investigators (Murray and Renard, 1891; Collet, 1905; Murray and Philippi, 1908; Cayeux, 1934 and Haughton, 1956) recovered phosphatic rocks from the Agulhas Bank between Cape Point and Port Elizabeth and established that at least some of the material was formed by replacement of calcium carbonate by calcium phosphate. They also recognised that the distribution of these rocks was associated with the nutrient-rich upwelled water and high biological productivity. A systematic survey of the Agulhas Bank enabled Parker (1971) to delineate the phosphorite deposit more accurately and to determine the dominant petrographic and geochemical characteristics of the rocks. Work by Parker (1971 and 1975) and Siesser (1971) established that the phosphatized limestones were formed by a micrite-to-collophane replacement mechanism involving permeating P-rich solutions (Parker and Siesser, 1972).

The main objectives of the present study are to establish the areal extent and composition of the phosphorite deposit and to determine how these rocks have affected the composition of the ambient unconsolidated sediment, thereby extending the type of work done by Parker (1971) and Summerhayes (1973) on the Agulhas Bank up the west coast of South Africa. Whole rock major element analyses were made of a representative number of phosphorites to (1) compare their geochemical composition with that of the Agulhas Bank samples and with adjacent onland phosphorites and (2) to provide background data to more specific microprobe investigations. Because the mineral constituents of phosphorite rocks are very inhomogeneous, even over extremely small (<1μm) areas, microprobe techniques were used to study the composition of individual minerals and elemental dispersion in the matrices. This assisted in elucidating the diagenetic processes involved in the formation of the carbonate-apatite minerals which form the bulk of the deposits.

4.4.2. Occurrence.

Phosphatic rock has been recovered from 60 stations off the Cape west coast. The location of these samples and the amount of rock recovered at each station are presented in Figure IV-5. As dredging was not carried out on a grid pattern, the location of these deposits will not represent the areal distribution of the phosphorite deposits accurately. To estimate the distribution of phosphorite occurrence better, the phosphorite stations have been plotted on a map depicting the approximate location of a rocky sea floor and the concentration of P_2O_5 in the unconsolidated sediment. The distribution of P_2O_5 (Fig.IV-5) in the sediment and the locations of the phosphorite stations clearly coincide. Dredging was carried out less frequently north of the Olifants River, which accounts for the smaller number of phosphorite samples in that area. These data suggest that the rocky areas of the mid and the

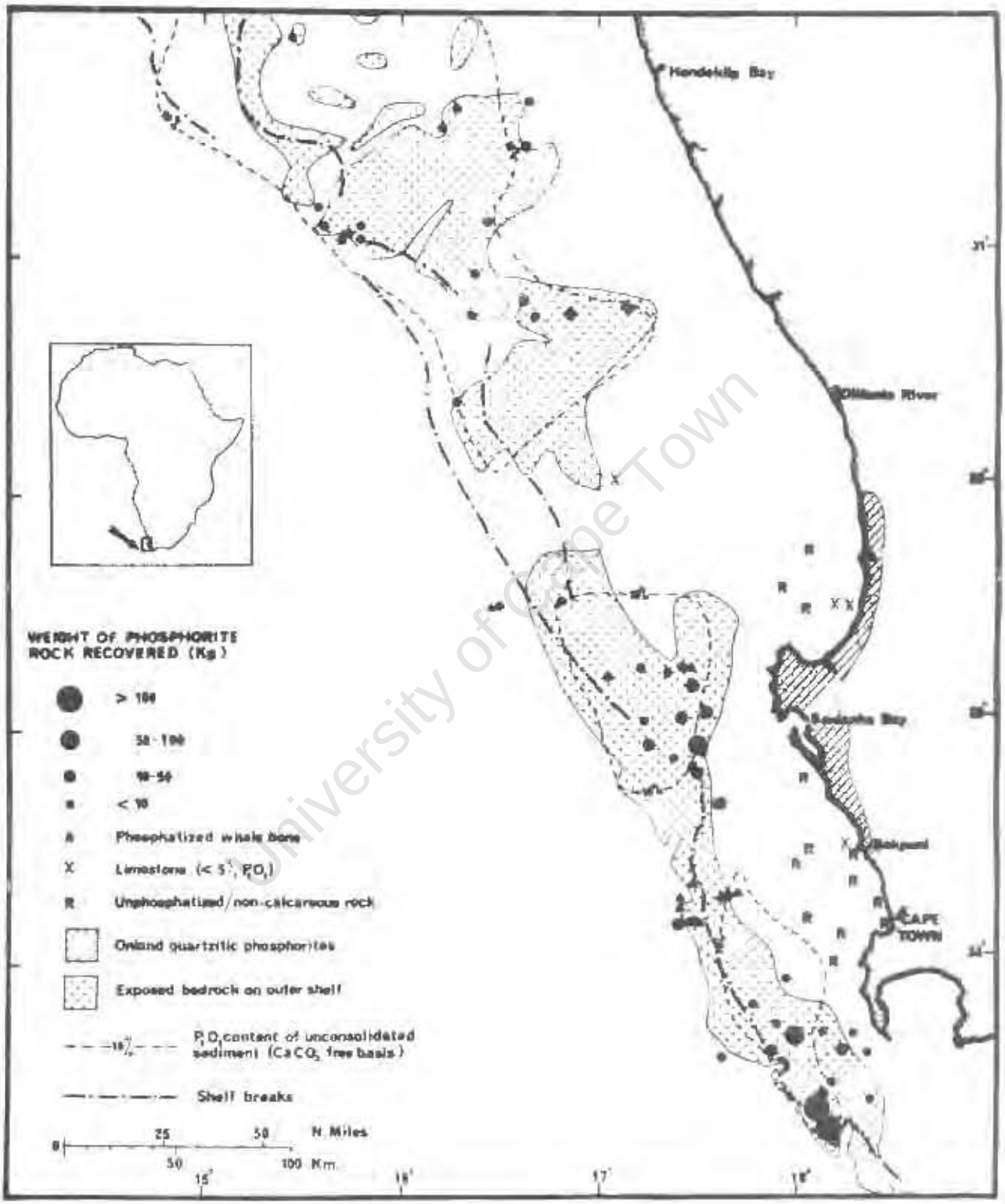


Figure IV-3

outer shelves are most likely to be phosphatic, especially as all rocks >5% P_2O_5 have been classified as phosphorites in this work. Rock on the shelf west of Lamberts Bay is buried by unconsolidated Quaternary sediments.

4.4.3. Classification of phosphorite types.

The same basic phosphorite classification used by Parker (1971) has been adopted in this investigation. His scheme comprises two conglomeratic and three non-conglomeratic classes. Phosphatized glauconite- and quartz-poor microfossiliferous limestones and their ferruginous equivalents constitute the NI and NII classes, respectively. Phosphorites composed of a poorly sorted mixture of quartz, glauconite and microfossils set in a micrite/collophane cement make up the third group (NIII) in Parker's non-conglomeratic class. The first conglomeratic class (CI) is characterized by abundant pebble inclusions (often NI phosphorite fragments) set in a matrix similar to a NIII phosphorite. The second conglomeratic class (CII) is similar to the first, but is distinguished by its low glauconite and high macrofossil abundance and an increased iron oxide content.

In this study, two subclasses have been added to Parker's basic classification to aid genetic interpretation. Phosphatized foraminiferal packstones (Siesser, 1971; Parker and Siesser, 1972) have been separated into a new subclass (NIA) to distinguish them from other microfossiliferous phosphorites (NIB) which contain abundant bryozoa and coralline algae. Parker's NIII phosphorites were described as containing abundant glauconite and almost no microfossiliferous pebbles. To avoid any ambiguity arising from this description, rocks in this class have been sub-divided into those which definitely do contain pebbles (NIIIB) and have therefore undergone some reworking, and those which contain no pebbles (NIIIA). An additional specification is that these pebbles, unlike those in the conglomeratic class, must have the same composition as that of the surrounding matrix. Glauconite-rich phosphatized limestones (ie. <5% P_2O_5), commonly containing abundant macrofossils, (often Pecten sp.) have been included in the classification under a separate class (GPL).

It is important to stress that this classification is subjective as all these rock types form part of a series. They range from nearshore terrigenous-rich phosphorites through mid-shelf glauconitic rocks to phosphatized deep-water foraminiferal limestones. The classification is designed merely to group together phosphatic rocks which were deposited under similar conditions and to indicate whether the rock has been subjected to reworking and transportation.

4.4.4. Petrography.

A petrographic study involving 117 thin sections was carried out on subsamples of all phosphorite types recovered from each of the 60 successful

dredge hauls.

The phosphorite off the Cape coast is similar in composition and external morphology to the Agulhas Bank phosphorites. The latter rocks have been described in detail by Parker (1971) and thus only a summary of the petrographic features of each group will be given in this section. Brief hand specimen and petrographic descriptions are presented in Appendix IV.

Glauconitic phosphate-rich limestones.

Glauconitic phosphate-rich limestones are usually yellowish-gray or pale olive and range mainly in size from very coarse pebbles to large cobbles. They frequently contain abundant macrofossils, including Pecten sp., and occasionally (No. 2248) phosphorite pebbles which partially account for their irregular shapes and rough, gritty surfaces.

Glauconite (5 to >50%) is always present, as the classification implies, and is commonly the dominant allogenic constituent. The glauconite pellets are medium sand-sized, well-rounded and may be distinctively oxidized. Other non-carbonate material in the rocks includes a variable amount of fine to very fine sand-sized angular quartz and minor feldspar. Foraminifera, mainly planktonic, constitute only a small proportion of the limestone (0-10%) and can even be absent. When present, they are frequently filled with glauconitic or phosphatic material. The micrite cement is sometimes altered to collophane, especially at the surfaces of the rock.

NI Phosphorites.

The largest number of samples belong to this group of phosphorites. NI phosphorites are yellow-gray to dusky brown and occur as very coarse pebbles or small cobbles. The rocks have rough surfaces and are mainly irregular in outline, though some are tabloid, or rounded (Plate IV-3).

Phosphorites assigned to this group contain a small (<5%) amount of glauconite and a variable (0-20%), but minor quantity of very fine sand-sized angular quartz grains. Foraminifera are the dominant component, but abundances vary markedly (5 to >50%). Planktonic species normally dominate over the benthic varieties, but the latter can be important locally. Agglutinated forms are also present in minor amounts. Foraminifera in these rocks, especially from north of the Olifants River, are usually filled with either glauconite or collophane. A test filled with glauconite is sometimes found adjacent (within millimetres) to one filled with collophane. The calcitic shells of foraminifera are often preferentially altered to glauconite. Macrofossils are more abundant in phosphorites from the Childs Bank region, but they are always subordinate to microfossils. Other biogenic materials include bryozoa, which can be important locally (e.g. off Cape Point), coralline algae, which are common in the shallower parts of Childs Bank area, and echinoderm plates and

spines.

Although many of the NI phosphorites contain >18% P_2O_5, the cement frequently appears to be more micritic than apatitic. Some samples (e.g. 313C) show increased phosphatization towards the edges or around holes bored by organisms (e.g. 310C). The cement in four rocks, at least one from each region, is partly glauconitic, and the cement from an additional two samples (2219 and 2266) is dominantly glauconitic. The origin and significance of this cement is discussed later. The abundant microfossils usually form a grain-supported texture and therefore these phosphorites are classified as packstones (Dunham, 1962).

NII Phosphorites.

Only one NII phosphorite was recovered and it is a moderate yellow-brown ovoid-shaped cobble.

The phosphorite assigned to this group resembles NI class varieties but contains no glauconite or quartz and only subordinate amounts (up to $\pm$10%) of planktonic and benthic foraminifera with minor echinoid and bryozoan fragments. NII phosphorite rocks are characterized by the presence of abundant brown Fe-rich cement.

NIII Phosphorites.

NIII phosphorites most frequently occur as grayish-green, olive-gray or dusky yellow-gray, very coarse pebbles with irregular and even knobbly surfaces (Plate IV-3).

Rocks of this class are rich (5 to >>50%) in medium sand-sized pellets of glauconite which are normally well-rounded. The pellets are usually mottled (see section 4.5.2.) and/or coated with apatitic rims, whereas brown oxidized grains occur only in restricted regions. Phosphorites of this class usually contain 5-10% very fine sand-size, angular quartz, but abundances vary markedly (<1 to 40%). Inshore samples (e.g. 1703 off the Cape Peninsula and 2239 off Saldanha Bay) may have a rich but very poorly sorted non-biogenic fraction, including rock fragments, feldspar and even jasper and chalcedony, but NIII phosphorites from farther off shore contain only silt-sized angular quartz grains. The frequent presence of rounded medium sand-size phosphorite grains in the matrix indicates at least one prior generation of phosphorite formation. Usually less than 5% foraminifera, mainly planktonic, occur in these rocks, but they are normally unfilled. An intimate mixture of delicate unbroken foraminifera, large angular quartz grains and rounded glauconite is an indication of the complex origin of some of these phosphorites. Macrofossils are found only in NIII phosphorites off Saldanha Bay. These components are almost always contained in a collophane cement, but small patches of glauconite and unaltered micrite are found.

The composition of the pebbles enclosed in NIIIB phosphorites is identical to that of the surrounding rock, so much so that their edges are sometimes hard to distinguish from the surrounding matrix.

CI Phosphorites.

These phosphorites are characterized by their conglomeratic texture, caused by the presence of abundant irregularly-shaped phosphatized pebbles (Plate IV-3).

Phosphorites assigned to this class are dusky yellow-orange, light olive-gray or yellow-gray and usually ovoid or tabloid in shape. They normally occur as cobbles with gritty, irregular and sometimes smooth surfaces.

The glauconite content (10-25%) of the matrix is similar to NIII phosphorite rocks. Fine to medium sand-sized glauconite pellets are usually well rounded, mottled and frequently coated with apatitic rims. The quartz content of the matrix never exceeds 20% (usually <5%) and foraminifera, predominantly planktonic and unfilled, only constitute <5%. The cement is collophane.

There are two types of enclosed pebble; one resembles NI class phosphorites and the other is similar to NIII phosphorite rocks. The former contains minor quartz (<5%) and glauconite (<5%), and mainly planktonic foraminifera (5-30%) which are usually filled with glauconite or collophane. The NIII-type pebbles contain more glauconite (10-20%) and quartz (5-15%), but less foraminifera (<5%), most of which are unfilled.

CII Phosphorites.

Only three CII phosphorite rocks were recovered, all from the Childs Bank region. Nodules of this class are characterized by an inhomogeneous conglomeratic texture produced by the presence of enclosed macrofossils, microfossiliferous pebbles and large fossil bone fragments. These rocks occur as orange or dark yellow-brown cobble-sized slabs with very irregular pitted surfaces, frequently exhibiting deep burrows produced by boring organisms.

The matrix contains minor glauconite (<5%) and quartz (<5%) and approximately 10-15% foraminifera. The foraminifera are predominantly planktonic and commonly filled with orange-coloured collophane (highly ferruginous, see section 4.4.9) and glauconite. Macrofossils, bone, and coralline algae are usually abundant. The cement is characteristically brown Fe-rich goethite and collophane, but minor amounts of glauconite cement are occasionally found.

The enclosed pebbles contain no glauconite or quartz and only 5-10%, mainly unfilled, foraminifera. The cement is typically goethite or collophane.

4.4.5. Distribution of phosphorite types.

Phosphorite rocks recovered from the Cape west coast appear to be concentrated roughly in three regions (Fig.IV-6): off the Cape Peninsula, west of Saldanha Bay, and north of the Olifants River. This grouping will be used for convenience when describing the distribution of the various phosphorite rock types.

Glauconitic phosphate-rich limestones (GPL)

These limestones occur mainly off Saldanha Bay, but samples have also been recovered from south of False Bay and off the Groen River where they occur as a minor porous secondary layering on phosphorite. These sediments are clearly younger than the phosphorites which they coat, and because of their faunal content and the presence of rounded oxidized glauconite grains, probably originated in a shallow-water environment.

NI Class phosphorites

Phosphatized pelagic-foraminiferal lime packstones have been recovered from all the phosphorite stations off the Cape Peninsula, and no areal distribution trends of NI phosphorites are apparent off Saldanha Bay. A significant feature of NI phosphorites off Saldanha Bay is the apparent tendency for micrite cement to be glauconitized rather than phosphatized. Only one sample off the Cape Peninsula (GiL-674) has glauconitic cement and no phosphorites north of Saldanha Bay exhibit this feature.

NIB phosphorites, containing mainly coralline algae, bryozoa, foraminifera and micrite are found on the mid shelf east of Childs Bank and on the flanks of the Bank itself. Phosphatized foraminiferal packstones (NIA) occur across the whole shelf north of the Olifants River.

NIIIA and NIIIB Class phosphorites

A 'conglomeratic' NIIIB phosphorite indicates reworking, but as the composition of the pebble inclusions is similar to that of the matrix, probably only minor transportation has taken place. It is difficult to note any significance in the distributions of these two types of glauconite-rich rock, as smaller pebble-free NIIIA phosphorites could probably be fragments of a larger NIIIB rock.

These phosphorite rocks occur across the shelf and upper slope off both the Cape Peninsula and off Saldanha Bay. The Saldanha Bay deposit is more glauconitic (average >50% glauconite) than the phosphorites off the Cape Peninsula (5-40% glauconite) and there appears to be a shorewards increase in the size and abundance of quartz in these rocks. Only two examples of this phosphorite type occur north of Saldanha Bay and both are relatively glauconite-poor (<5% of the total rock).

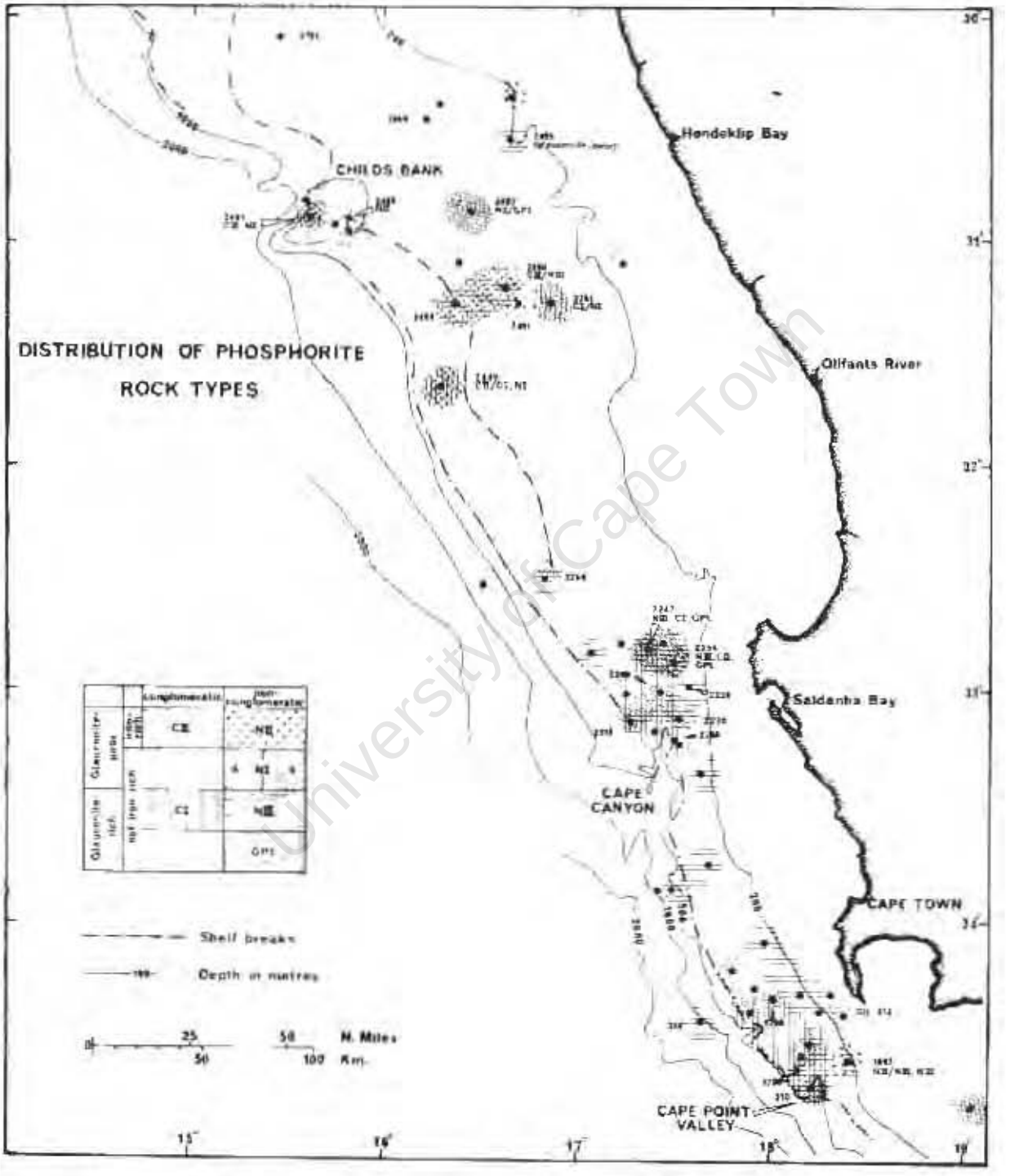


Figure IV-6

CI Class phosphorites

Glauconite-rich conglomeratic phosphorite (CI) occurs on the outer shelf off the Cape Peninsula and covers most of the shelf west of Saldanha Bay. On average the Saldanha Bay CI phosphorites are more glauconitic and less quartzitic than those off the Cape Peninsula, and like the NIII phosphorites, they are almost completely absent from the northern region.

Ferruginous phosphorites (Classes NII and CII)

Only one ferruginous phosphorite sample has been recovered from south of Saldanha Bay (in the Cape Point Valley), but there is a marked increase in abundance (8 stations) of ferruginous phosphatic rocks north of the Olifants River. North of Saldanha Bay, geothite replaces glauconite as the common iron-bearing mineral.

4.4.6. Relationship between phosphatic rocks and the ambient unconsolidated sediment.

(a) Phosphate (as P_2O_5) in the phosphatic rocks and unconsolidated sediments.

The highest phosphate values in the unconsolidated sediment coincide with the distribution of phosphorite rock (cf. Summerhayes, 1972, for the Agulhas Bank sediments). Also the change in the type of phosphorite rock north of Saldanha Bay is reflected in the unconsolidated sediment. NI and NIII phosphorite gravels and sand-size grains are common off the Cape Peninsula and west of Saldanha Bay, but NII fragments and foraminiferal infillings are the most characteristic constituents of authigenic sediments to the north.

The phosphate content of the unconsolidated sediment, on a $CaCO_3$-free basis, is greatly enriched north of Saldanha Bay (20 to 40% as compared to 10-20% to the south (Fig.IV-7), but the average phosphate values of the rock from the three areas are almost the same (19,11% P_2O_5 off the Cape Peninsula, 19,58% west of Saldanha Bay and 19,8% in the northern area, Figure IV-7). The apparent phosphate depletion of unconsolidated sediment in the north is therefore due only to a dilution effect created by greatly increased carbonate sedimentation north of Saldanha Bay (Summerhayes et al., 1973).

(b) Glauconite in the phosphatic rocks and in the unconsolidated sediments.

It was previously believed that the glauconite deposits were probably a continuous mid-shelf feature along the entire west coast. It was thought that areas low in glauconite were diluted by abundant biogenic sedimentation or were buried by Quaternary terrigenous detritus. However, the glauconite content of the phosphatic rock, from which the authigenic minerals are derived (Birch, 1971 and Summerhayes et al., 1973), indicates that this supposition is not entirely true and that definite areas of glauconitization existed on the shelf. Phosphatic rocks and unconsolidated sediment off the Cape Peninsula

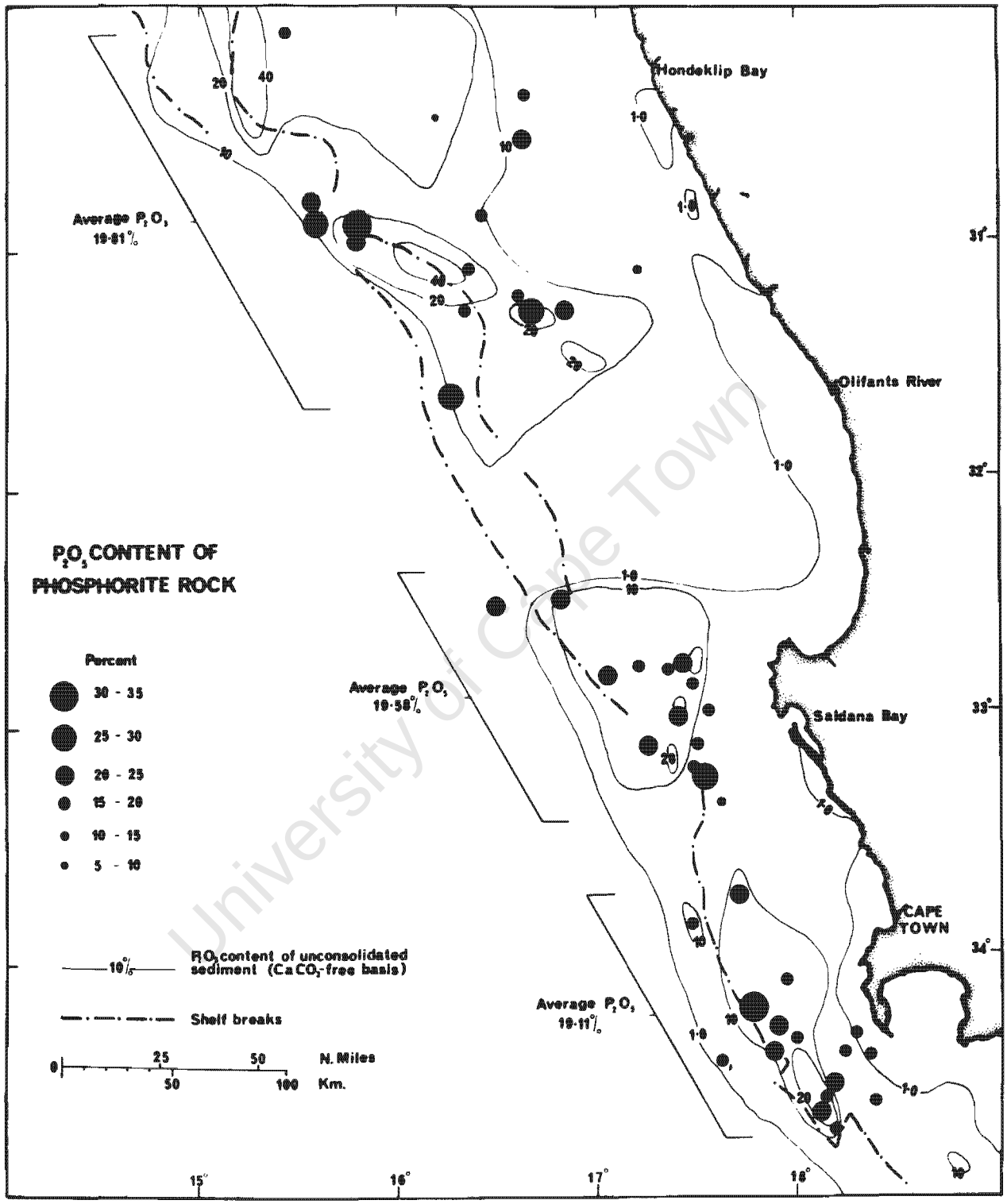

Hondeklip Bay
Olifants River
Saldana Bay
CAPE TOWN
Average P_2O_5 19·81%
Average P_2O_5 19·58%
Average P_2O_5 19·11%
P_2O_5 CONTENT OF PHOSPHORITE ROCK
Percent
30 - 35
25 - 30
20 - 25
15 - 20
10 - 15
5 - 10
P_2O_5 content of unconsolidated sediment ($CaCO_3$-free basis)
Shelf breaks
N. Miles
Km.
31°
32°
33°
34°
15°
16°
17°
18°

Figure IV-7

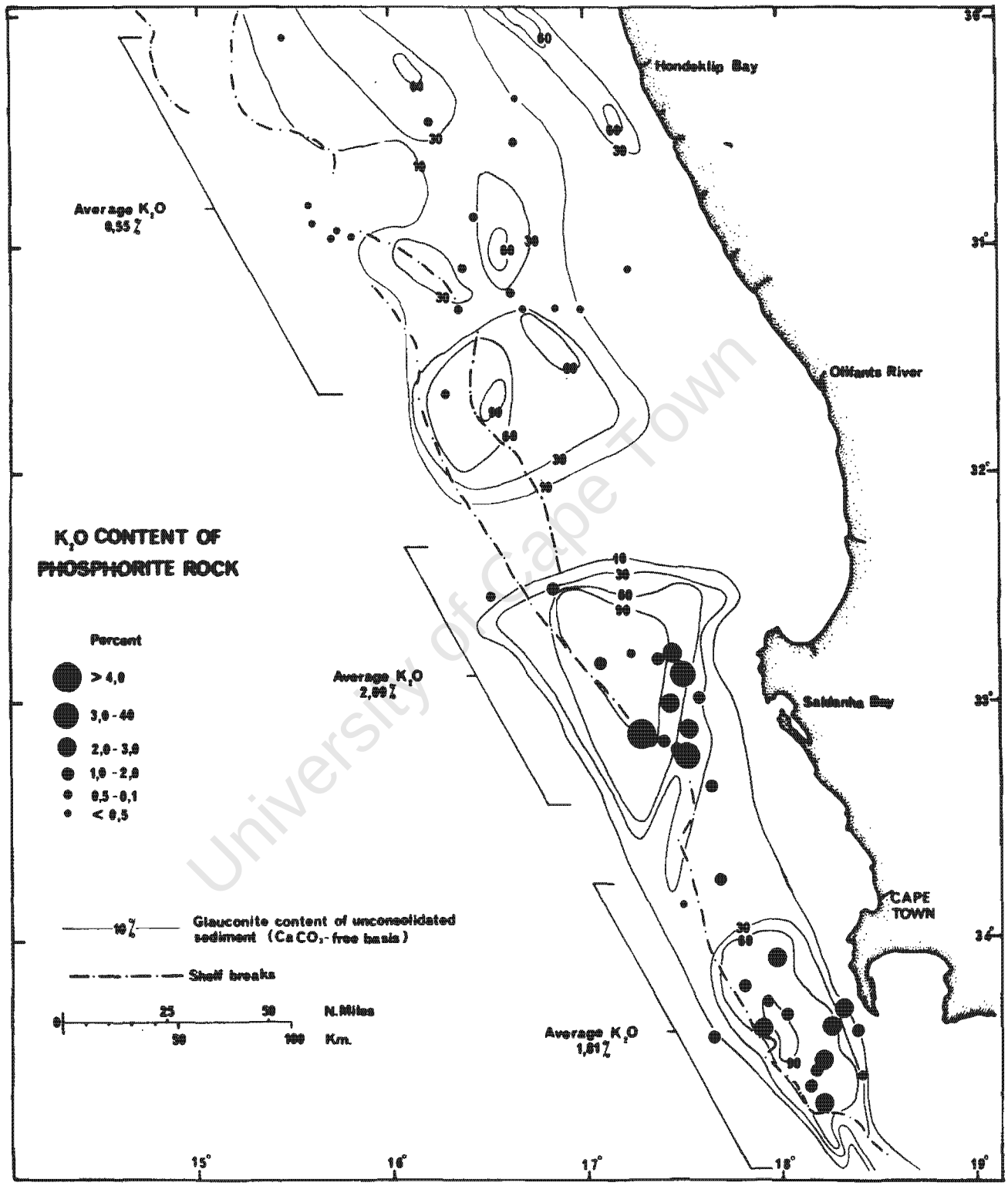

Hondeklip Bay
Olifants River
Saldanha Bay
CAPE TOWN
Average K_2O 0,55 %
Average K_2O 2,89 %
Average K_2O 1,81 %
K_2O CONTENT OF PHOSPHORITE ROCK
Percent
> 4,0
3,0 - 4,0
2,0 - 3,0
1,0 - 2,0
0,5 - 0,1
< 0,5
10 % Glauconite content of unconsolidated sediment ($CaCO_3$-free basis)
Shelf breaks
25 50 N.Miles
50 100 Km.
15°
16°
17°
18°
19°
31°
32°
33°
34°

Figure IV-8

and off Saldanha Bay contain abundant glauconite, and phosphorites have high K_2O values (average 1,81% K_2O and 2,0% K_2O respectively (Fig.IV-8)), but phosphorites and unconsolidated sediments from the northern area are relatively poor in glauconite (average K_2O value of phosphorites in this region is 0,55%). A small, glauconite concentration (max. 60% glauconite) in the unconsolidated sediment off the Olifants River can be related to a glauconite-rich secondary coating of NIII phosphorite on the phosphatic rocks in this area.

The lower glauconite values in the unconsolidated sediments in the region north of the Olifants River are therefore likely to be real as the phosphorites from which they are derived are also depleted in this mineral.

4.4.7. X-ray diffraction studies.

X-ray diffraction analyses of 15 phosphorites selected from each of the five phosphorite classes were undertaken to identify the minerals present in the rock and to determine the nature of the phosphate phase, including its CO_2 content.

(a) The mineralogy of the phosphorite rocks.

The diffractograms of the phosphorite rock (Fig.IV-9) from the different classes are characterized by variations in the abundance of the four dominant mineral phases present ie. collophane, calcite, quartz and glauconite. NI, NII and CII phosphorites produce very similar X-ray traces, all being dominated by abundant calcite. NIII and CI phosphorites are also similar and are characterized by abundant quartz and the presence of a glauconite reflection at 10Å (significant contamination by illite which also produces a reflection at 10Å is discounted on petrographic evidence).

Mixed-layer clays (possibly immature glauconite) were present in almost all phosphorites, but kaolinite was found only in trace amounts in four samples (1706, 2703, 2240 and 2460). Plagioclase feldspar is present in all the samples and K-feldspar occurs in only three samples (1692, 1700 and 1706), all from off the Cape Peninsula.

Diffractograms of NI, NII and CII phosphorites are similar and X-ray traces of NIII and CI class phosphorites closely resemble one another. Diffractograms of NI and NIII phosphorites are presented in Figure IV-9. The X-ray traces for all phosphorites, except the NII class, show sharp, well-defined peaks which suggest that the apatite mineral is well crystallized. The NII phosphorite produced more diffuse reflections, an aspect also observed by Parker (1971) who suggested that the apatite of NII phosphorite rocks was not so well crystallized.

(b) The mineralogical nature of the phosphate phase.

The equivalent d-spacings for a typical phosphorite (2254 NIII) from the Cape west coast are presented alongside those of a phosphorite from the

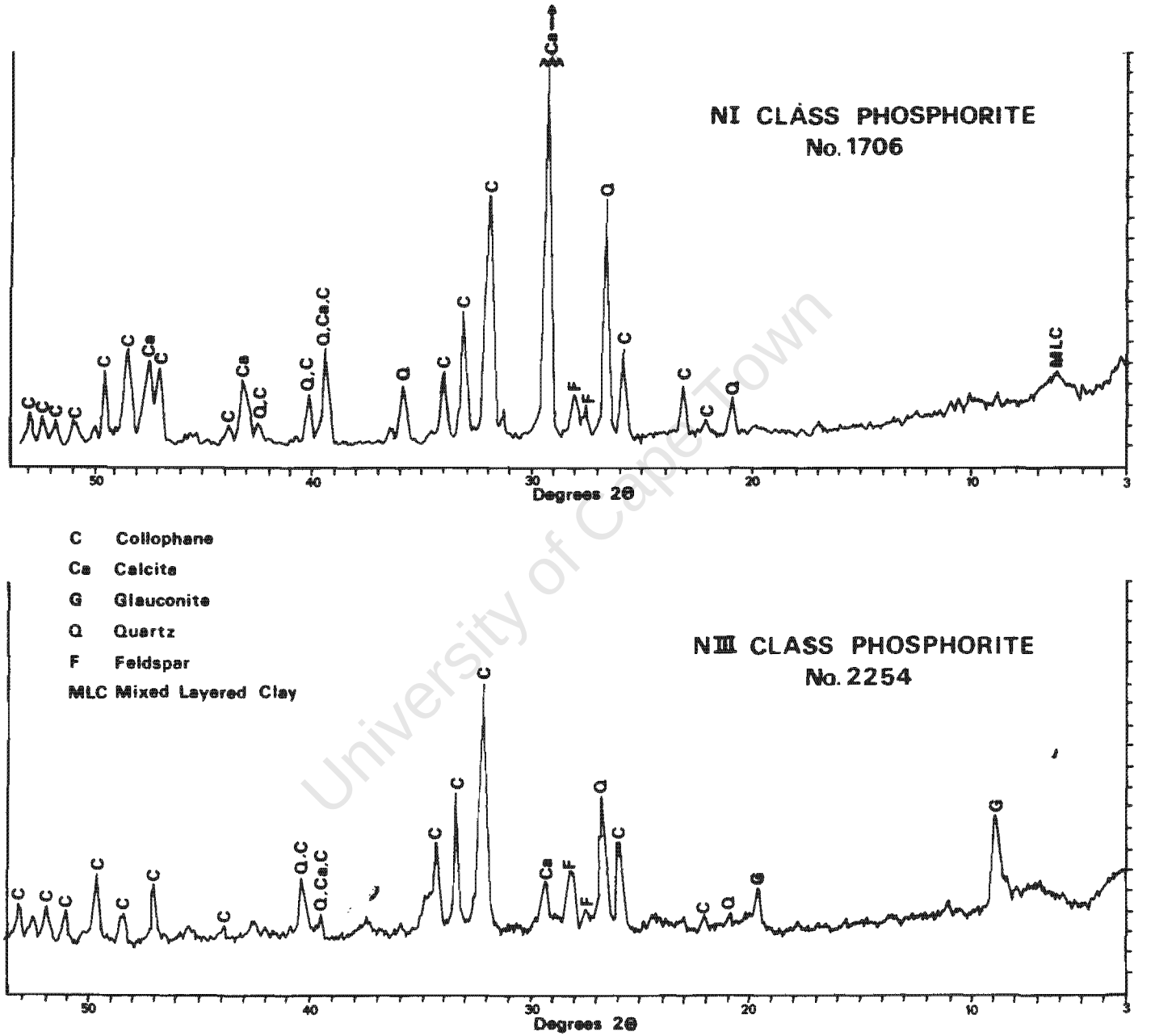


Figure IV-9

Table IV-2. X-ray diffraction data for onland and off-shore apatites.

hkl	Agulhas Bank phosphorite (1) d(Å)	N Carolina pellets (2) d(Å)	This investigation				
			offshore phosphorites		onshore phosphorites		
			NI type d(Å)	NIII type d(Å)	Quartzitic phosphorite SITE-1. d(Å)	Phosphatized coquina SITE-6. d(Å)	Varswater pelletal phosphorites (3) d(Å)
200	4,04	-	4,04	4,04	-	4,04	-
111	3,85	-	3,85	-	-	3,87	-
002	3,45	3,45	3,45	3,44	3,44	3,44	3,44
102	3,17	3,16	3,17	3,16	3,15	3,18	3,17
120,210	-	3,06	-	-	3,06	3,07	3,06
121,211	2,79	2,79	2,80	2,79	2,79	2,80	2,79
112	2,77	2,78	2,78	2,77	2,77	2,77	-
300	2,69	2,70	2,71	2,69	2,70	2,70	2,70
202	2,62	2,62	2,63	2,62	2,62	2,62	2,62
122,212	2,28	2,29	2,29	2,28	2,28	2,28	2,36
130,310	2,24	2,24	2,24	2,24	2,23	2,23	2,23
131,311	2,12	2,13	2,11	2,12	2,12	2,13	2,13
113	2,06	2,06	2,06	2,06	-	2,07	2,06
203	-	1,996	-	1,995	-	-	1,992
222	1,930	1,932	1,935	1,928	1,933	1,940	1,924
132,312	1,877	1,875	1,881	1,877	1,881	1,888	1,879
123,213	1,836	1,835	1,842	1,835	1,835	1,838	1,830
231,321	1,788	1,789	1,791	1,788	1,796	1,782	1,791
140,410	1,762	1,763	1,768	1,762	1,768	-	1,763
402	1,743	1,738	1,731	1,738	1,746	1,747	1,746
004	1,725	1,723	-	1,722	1,722	1,721	1,721
232,322	-	-	-	1,719	-	-	1,629

(1) Parker, 1971
(2) Rooney and Kerr, 1967
(3) Tankard, 1974(b)

Agulhas Bank (Parker, 1971) in Table IV-2. The values are almost identical which suggests that the prime phosphate mineral present in phosphorites from the Cape coast is francolite, a variety of carbonate fluorapatite (Parker, 1971).

(c) The CO_2 content of the apatite phase.

Although the function of the CO_3^{-2} radical in the apatite structure is not completely understood (Tooms et al., 1969), it is nevertheless generally considered (McConnell, 1952; Altschuler et al., 1958; Rooney and Kerr, 1967 and McClellan and Lehr, 1969) to be present as an integral part of the apatite lattice through substitution for the PO_4^{-3} radical (McConnell, 1952 and 1960). The CO_2 content of the apatite phase was determined using the peak-pair method described by Gulbrandsen (1970) to establish the extent of CO_3^{-2}/PO_4^{-3} substitution which has taken place.

The average CO_2 content of the apatite mineral (5,5%) in the phosphorites from the Cape west coast is the same as that given by Parker (1971) for the Agulhas Bank deposits, but the range of values (4,8 to 6,1) is slightly larger than that obtained by him. The values for the pelletal phosphorite samples (3,7 and 3,9% CO_2) are very similar to those of the pelletal phosphorites off South West Africa (3,49% CO_2) as reported by Bremner (1975(b)), but the CO_2 content of the apatite filling foraminifera in the Childs Bank region is lower than that determined by Rogers (pers.comm.) for the same material in the adjacent area to the north (3,4% as opposed to 5,2% CO_2).

It appears that the apatite in phosphorite rock from the highly calcareous sediments on the Agulhas Bank and off the Cape west coast is rich in CO_2, but that the apatite of pelletal phosphorites in the carbonate-poor sediments off South West Africa is depleted in CO_2. Intermediate values (5,8 and 5,3% CO_2) determined by Rogers (pers.comm.) for pelletal phosphorite from carbonate-poor sediments off Sylvia Hill, as well as high (6,0% CO_2) values presented by Baturin (1969) for South West African and Chilean (Baturin and Pevelin, 1972) nodules and concretions indicate that the relationship between the CO_2 constituent of the apatite phase and the carbonate content of the ambient sediment is doubtful.

A regional increase in the CO_2 content of the Phosphoria apatites is considered by Gulbrandsen (1970) to be due to an increase in the water temperature. This implies that the phosphorites from the Cape west coast and Agulhas Bank were formed in warmer waters than the pelletal material from off South West Africa and that both these deposits originated in water warmer than that of the Phosphoria apatites. However, evidence of high-CO_2 apatites in Recent concretions in sediments beneath the cold upwelled waters off South West Africa (Baturin, 1969) does not appear to support this supposition. Recently Dr. McArthur of the Department of Earth Sciences, University

of Leeds, has shown that the apatite CO_2 content is most probably a weathering function and does not represent the depositional environment (Summerhayes, pers.comm.).

4.4.8. Whole rock geochemical analyses.

Major element analyses of 15 phosphorites from the Cape west coast were made to establish the geochemical characteristics of the various phosphorite classes described earlier, and to compare them with the same rock types from the Agulhas Bank. The average chemical composition of the Cape west coast phosphorites is compared with similar rocks from other localities, including the local adjacent onland deposits.

(a) Geochemical characteristics of the five phosphorite classes.

The chemical composition of the phosphorites from the Cape west coast is presented in classes alongside those from the Agulhas Bank in Table IV-3. The values for the various classes from the two regions are very similar, except that the Fe-rich varieties (NII and CII) from the Agulhas Bank are more ferruginous.

As found by Parker (1971), the chemical composition of the phosphorites is mainly related to variations in the abundance of the dominant mineral phases present in each group, e.g. quartz, calcite, glauconite and collophane. Thus the NI class which contains abundant calcareous debris and some unaltered micrite cement is characterized by high CaO values, but low K_2O, SiO_2 and Fe_2O_3. The NIII group on the other hand, is characterized by high K_2O and SiO_2 owing to an abundance of glauconite and negligible calcitic material. High Al_2O_3, Fe_2O_3 and MgO are probably also a reflection of the enrichment of this mineral phase. Although some of the Al_2O_3 and SiO_2 must reside in the feldspar minerals detected in the X-ray diffraction investigation, low Al_2O_3/K_2O figures for the NIII and CI classes indicate that only minor "non-glauconite" Al is present, and high Al_2O_3/K_2O values for NI, NII and CII phosphorites suggest that a significant amount of Al resides in non-glauconitic minerals, probably mainly clay minerals and feldspar, both of which were detected in X-ray diffractograms. The composition of the CI class phosphorites is very similar to the NIII varieties, mainly because of the abundant glauconite and minor calcite they both contain. The elements (SiO_2, Al_2O_3, K_2O and Fe_2O_3) associated with the glauconite phase are reduced in the CI phosphorites owing to dilution by inclusions of non-glauconitic NI pebbles.

Of the ferruginous phosphorites (NII and CII), only the NII variety contains relatively high Fe (11% Fe_2O_3) and this enrichment is considerably less than for the Agulhas Bank phosphorites of the same class. However, this Fe content signifies a six times enrichment over that of NI phosphorites which have a similar composition and because of the essentially non-glauconitic nature of these rocks, it implies that most of the Fe is associated with the authigenic

Table IV-3. Major element composition of the five phosphorite classes from the Agulhas Bank and the Cape West coast.

	NI		NII		NIII		CI		CII		CI + CII	COMPOSITE	AVERAGE	
	CWS(1)	AB(2)	CWS	AB	CWS	AB	CWS	AB	CWS	AB	CWS	CWS	CWS	AB
No.of Samples	4	3	1	3	4	3	3	8	1	4	4	2	15	21
SiO_2	4,42	6,20	12,06	3,45	24,81	21,05	19,76	15,30	13,94	13,79	18,30	5,64	13,44	12,84
TiO_2	0,08	0,06	0,12	0,04	0,13	0,16	0,11	0,10	0,13	0,11	0,12	0,08	0,11	0,12
Al_2O_3	1,12	1,13	2,05	0,92	2,45	2,36	1,89	2,14	1,47	2,12	1,79	1,21	1,70	1,85
Fe_2O_3	1,69	1,40	11,11	25,80	6,06	5,83	5,17	5,58	5,24	7,34	5,19	4,01	5,55	8,24
MnO	0,02	0,01	0,04	0,06	0,01	0,01	0,01	0,01	0,05	0,02	0,02	0,02	0,03	0,02
MgO	1,04	0,97	1,17	1,49	1,69	1,50	1,46	1,34	1,72	1,45	1,52	0,65	1,29	1,35
CaO	46,83	47,02	37,67	33,42	31,33	33,14	33,98	37,04	40,82	36,54	35,69	44,98	39,27	37,29
Na_2O	1,09	0,62	0,96	0,36	0,88	0,69	1,18	0,78	0,67	0,73	1,06	1,11	0,98	0,67
K_2O	0,44	0,43	0,57	0,39	2,50	2,02	2,01	1,57	0,91	1,51	1,74	0,70	1,19	1,29
P_2O_5	18,76	14,82	15,42	10,26	17,86	18,05	18,92	17,89	15,41	16,82	18,05	20,63	17,83	16,18
L.O.F.	21,49	25,52	19,02	23,24	11,94	12,70	14,07	16,15	20,48	16,89	15,68	20,18	17,86	18,15
TOTAL	99,13	98,18	99,31	99,43	99,66	97,51	98,55	97,90	100,84	97,32	99,16	99,67	99,53	98,00
F	2,57		2,10		2,06		2,54		2,22		3,17	3,29	2,46	2,10
C_{org}	0,52	-	0,31	-	0,54	-	0,64	-	0,11	-	0,48	0,46	0,43	-
CaO/P_2O_5	2,55	-	2,44	-	1,76	-	1,80	-	2,65	-	1,97	2,18	2,23	2,30
Fe/P_2O_5	0,14	0,14	0,14	0,14	0,12	0,12	0,14	0,124	0,14	0,121	0,14	0,20	0,14	0,130
Al_2O_3/K_2O	2,62	-	3,60	-	1,29	-	0,98	-	1,62	-	1,16	1,79	1,98	1,43

(1) Cape western shelf

(2) Agulhas Bank phosphorites

goethite component. Although only one sample from each of the NII and CII classes was analysed, their compositions showed the same relationships to the other groups as those found on the Agulhas Bank. The Fe content of the CII phosphorite from the Cape west coast is less than that of the NIII and CI classes, but is twice that of the equivalent non-glauconitic NI variety. These Fe-rich varieties are clearly characterized by being relatively enriched (3 to 4 times) in MnO compared with the other groups, which according to Parker (1971) is due to the scavenging action of "non-glauconitic" Fe in the matrix. The inclusion of calcareous debris and microfossiliferous pebbles in the NI, NII and CII phosphorites can be observed in the increased CaO/P_2O_5 compared with the glauconitic varieties (NIII and CI).

Because such a large number of rocks comprising more than one class was recovered, especially from the Childs Bank area, two composite samples were included in the geochemical investigation. The composition of these samples proved to be very similar to the average CI composition.

(b) The geochemical composition of phosphorite from the Cape west coast compared with phosphorites from other localities.

The average chemical composition of the phosphorites from the Cape west coast together with averages for phosphorites from other localities are given in Table IV-4.

The average compositions of the Agulhas Bank and Cape west coast phosphorites are almost identical, except that the Agulhas Bank rocks are more ferruginous. This is partly due to a higher proportion of ferruginous samples selected for the Agulhas Bank investigation. These geochemical and petrographical data indicate that the phosphorites from the Cape west coast can be regarded simply as an extension of the Agulhas Bank deposit.

Variations in the average composition of the phosphatic material from different localities are mainly a reflection of variations in the nature and degree of dilution caused by the non-phosphatic components in the deposit. For example, the depletion in P_2O_5, CaO and enrichment in SiO_2, Al_2O_3, Fe_2O_3, MgO, Na_2O and K_2O in phosphorites from the Cape west coast with respect to the Phosphoria deposits, merely indicates increased quartz, glauconite and calcite dilution in the former, ie. a purely sedimentological feature. Similarly, a comparison of the CaO/P_2O_5 values for phosphorites from NW Africa with the Cape coast material indicates that both deposits are being diluted by calcite, and an equally high CaO in the Phosphoria phosphorite is due to less dilution and subsequent enrichment in apatite.

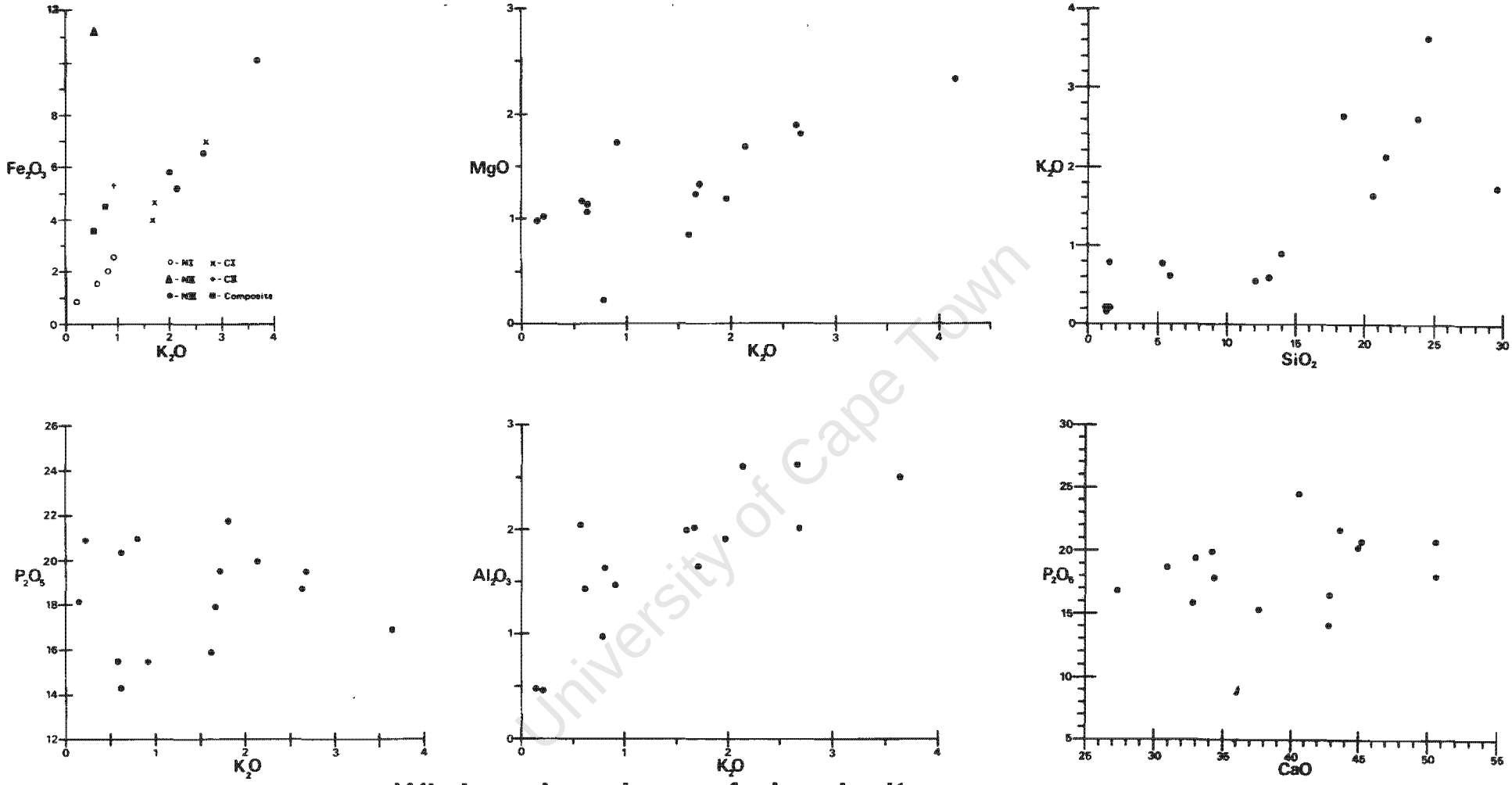
(c) Inter-element relationships.

The major constituents of these phosphorite rocks are quartz, calcite, collophane and glauconite. Ca can be assigned to both calcite and collophane,

Table IV-4. Average major element composition of phosphates from various localities (Whole rock determinations)

	This work (15 analyses)	Agulhas Bank (21 analyses) (1)	N.W. Africa (11 analyses) (2)	Phosphoria formation (60 analyses) (3)
SiO_2	13,44	12,84	6,73	11,9
TiO_2	0,11	0,12	0,08	0,1
Al_2O_3	1,70	1,85	-	1,7
Fe_2O_3 (4)	5,55	8,24	4,30	1,1
MnO	0,03	0,02	0,06	<0,01
MgO	1,29	1,35	3,29	0,03
CaO	39,27	37,29	31,16	44,0
Na_2O	0,98	0,67	-	0,6
K_2O	1,19	1,29	0,73	0,5
P_2O_5	17,83	16,18	16,96	30,5
F	2,46	2,10	-	3,1
F/P_2O_5	0,140	0,130	-	0,102

(1) Parker, 1971
(2) Summerhayes, 1970
(3) Gulbrandsen, 1966
(4) Total Fe



Whole rock analyses of phosphorite

Figure IV-10

but the poor co-variance between Ca and P_2O_5 (Fig.IV-10) suggests that a significant proportion of the Ca in these rocks is unrelated to collophane. This "non-phosphatic" Ca is probably mostly related to the unaltered carbonate phase, especially in the NI phosphorite rocks. There is also a general increase in SiO_2 with K_2O, but again the spread of values indicates that a large amount of the Si is not related to the glauconite phase and is probably mostly present as a quartz or possibly as feldspar and clay minerals. The poor co-variance between the elements contained mainly in the glauconite can be ascribed to the "masking" effect of other Mg; Al; Fe-bearing mineral phases in the rock (cf. Fig.IV-3). However, the plot of Fe_2O_3 vs K_2O indicates that most of the Fe in the NI, NIII and CI phosphorites is associated with the glauconite mineral, whereas in the non-glauconitic NII and CII phosphorites the Fe is unrelated to the K_2O content.

Microprobe studies of single mineral phases and of phosphorite matrices eliminates much of this dilution effect and inter-element relationships become more meaningful.

4.4.9. Microprobe studies of phosphorite rocks.

Phosphorite rocks contain materials derived from diverse sources, for example terrigenous quartz, biogenic calcite and authigenic collophane and glauconite. Thus micro-analytical techniques are essential if the genetic significance of the individual phases is to be studied. The electron-beam scanning and micro-analytical facilities of the microprobe were used to investigate the dispersion of the two main authigenic minerals (glauconite and collophane) in the phosphorites and to determine the composition of individual inclusions (e.g. phosphate pellets and foraminiferal infillings) or selected areas (10-15µm in diameter) within the matrix.

(a) The phosphorite matrix.

Petrographic investigations revealed that in plane polarized light, the colour of the phosphorite matrix appeared either colourless, dark brown, or lime-greenish brown to lime green. The entire matrix of some rocks comprised exclusively colourless or lime-green material, but brown and lime-greenish brown varieties were more frequently intimately associated in the same rock. The lime-greenish brown variety occurred as the cement for the "ghost" pebbles within the matrix of NIIIB phosphorites, or as small pockets (Plate IV-5) between grains within the dark brown matrix of NIII and CI phosphorites. In some NIII phosphorites it occurred as the dominant cement variety. The contact between the different matrix types is always distinct (Plate IV-5) and the various varieties never merge into one another.

Results of 21 analyses indicate that the collophane cement is always diluted by a varying amount of non-phosphatic material and that the K_2O content

increases as the colour changes from brown to green. It must be pointed out, however, that the size of the spot being analysed in this study varied between 10 and 15μm for different determinations and this implies that the cement is composed of a finely (often <4μm) disseminated mixture of several minerals. Although the most homogeneous areas were selected for analysis, the composition of the matrix varies markedly as is indicated below in the range in values obtained:

SiO_2	Al_2O_3	Fe_2O_3	K_2O	MgO	Na_2O	CaO	P_2O_5
28,69	3,73	10,97	3,22	2,12	1.86	30,25	30,77
3,40	0,57	0,48	0,18	0,49	0,30	49,87	19,83

Although the proportion of diluents varies markedly, the brown matrices always contain the lowest K_2O values (<1%) and the darkest green varieties contain up to 3,2% K_2O. The K_2O content of the colourless matrix is irregular, but it is characterized by unusually high CaO and P_2O_5 values (Table IV-5).

It is evident from the relationship between K_2O and P_2O_5 (Fig.IV-11) that collophane (Ca,P) and glauconite (K, Si, Mg, Al) are the two dominant minerals comprising the cement. Clay minerals, other than glauconite, are not expected to contribute significantly to the matrix analyses as indicated by the X-ray diffraction studies and by the similarity in the inter-element relationships of the pure glauconite phase and of the glauconite component of the matrix. All the CaO is related to the phosphate phase, but an inconsistent Na_2O vs P_2O_5 relationship indicates that some of the Na is associated with other phases within the matrix, probably feldspar (Na substitution in the apatite structure is discussed later). All the MgO and most of the Fe_2O_3 in the cement is associated with the glauconite phase as is indicated by the covariance of these elements with K_2O (Fig.IV-11). A plot of Fe_2O_3 vs K_2O indicates that Fe is occasionally present in the cement in excess of the structural requirement for glauconite. This "non-glauconite" Fe occurs as light orange streaks within the phosphorite matrix. Most of the Si in the cement is associated with the glauconite, but high irregular SiO_2 values in the K_2O-poor brown cement indicates that either clay minerals or silt-sized quartz is present. The former is thought more likely as Al is often present in the cement in excess of its structural requirement in the glauconite structure.

(b) Evidence for glauconite and phosphate solutions in phosphorites.

Phosphatic and/or glauconitic material can fill fractures in the matrix of NI phosphorites or cracks in quartz grains as well as cavities surrounding pebbles in some conglomeratic phosphorites. Two examples are presented below to illustrate the manner in which this material is deposited.

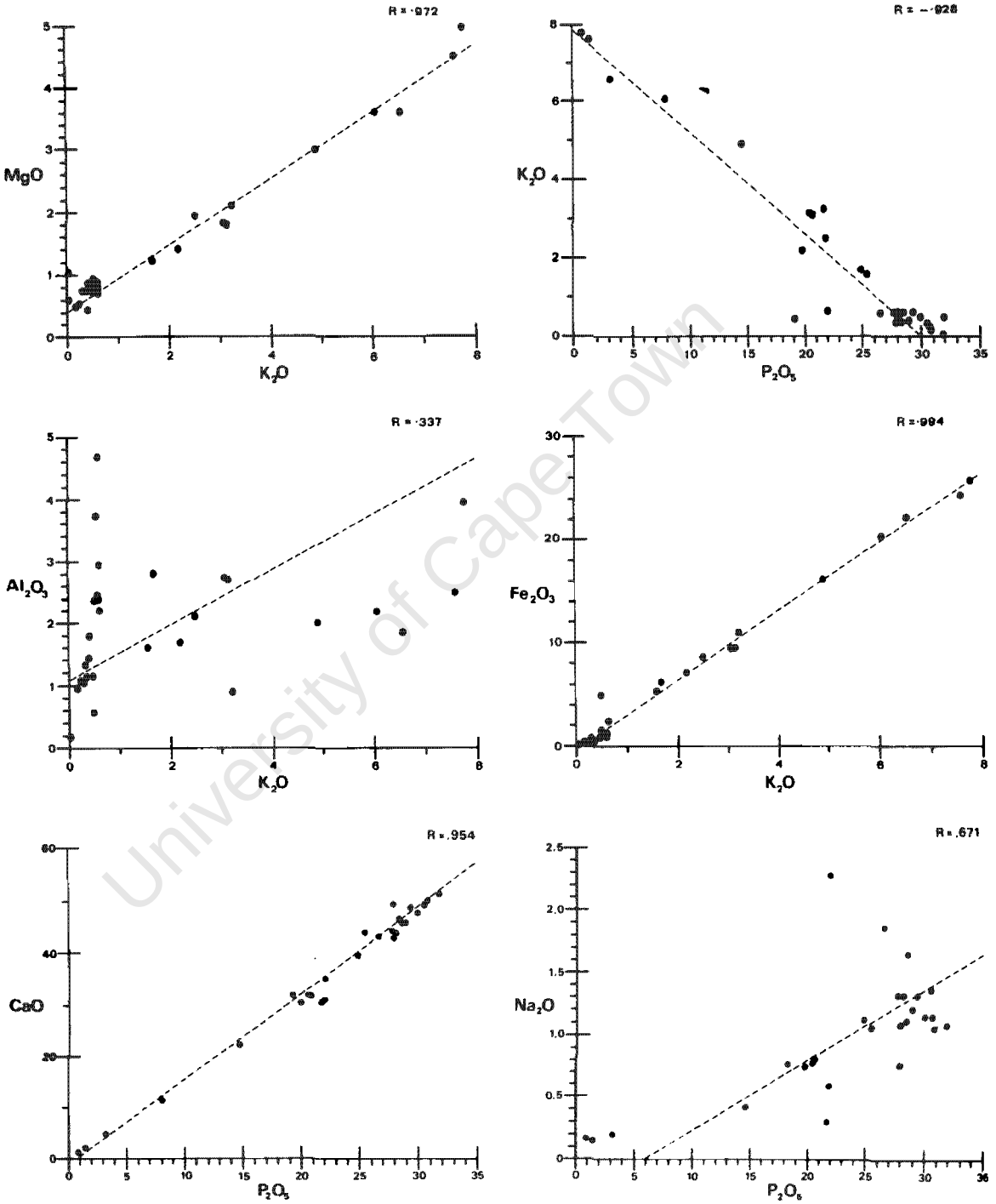
Glauconite was initially deposited on the walls of the fracture presented in Plate IV-6. The vein which occurs in the phospho-glauconitic matrix of

Table IV-5. Micro-analyses of phosphatic matrices and foraminiferal infillings in phosphorites.

	Phosphatic Matrices					Foraminiferal infillings	
	light brown	lime-green	colour-less	high silica	all matrices (2)	phosphatic	ferruginous phosphatic
No. of Samples	10	4	3	4	17	5	4
SiO_2	7,06	20,18	6,95	21,10	10,13	5,49	8,19
Al_2O_3	1,98	2,19	1,62	2,36	1,96	1,85	5,01
Fe_2O_3 (1)	1,40	7,79	2,39	1,09	3,08	3,87	35,16
MgO	0,81	1,53	0,75	0,69	0,97	0,98	1,67
CaO	46,20	34,36	46,14	38,77	43,41	45,64	24,31
Na_2O	1,32	0,85	1,10	1,25	1,17	0,98	0,77
K_2O	0,51	2,50	0,70	0,50	1,01	0,70	0,87
P_2O_5	28,93	21,58	28,75	24,35	27,17	27,06	16,20
Total	88,21	91,73	88,40	90,11	88,90	86,57	92,18

(1) Total Fe

(2) Excluding high silica matrices.



Microprobe analyses of phosphorite matrices

Figure IV-11

an NI phosphorite was subsequently filled by alternating layers of glauconitic and phosphatic material in a manner which is similar to the foraminifera infilling seen in Plate IV-17. The vein is deflected around thin-walled foraminiferal tests within the matrix, suggesting that the fracturing occurred at a time when the matrix was not yet fully solidified. Phosphorite containing abundant glauconite grains (NIII class) was later laid down over this deposit during a separate authigenic episode.

Another example of glauconitic/phosphatic solutions permeating through phosphorite rocks can be seen in Plate IV-7. The Plate shows that vacant spaces between NI pebbles in a CII phosphorite rock were filled by almost pure glauconitic and phosphatic material. There is no evidence of alternating glauconitic and phosphatic layering in the material such as occurs in the previous example, and from the fracture pattern in the glauconitic vein at its contact with the phosphatic vein, it seems that the materials were intruded in a plastic state during closely separated episodes.

It is evident from these examples that glauconite and apatite were precipitated from solutions into fractures and vacant spaces in phosphorites during or shortly after lithification and that in some cases these phases are closely associated.

(c) The collophane phase.

The major element data obtained from the whole rock analyses and from the probe investigations of the cement are not suitable for studying the collophane phase because of the presence of abundant non-phosphatic material. However, because both F and P_2O_5 are primarily associated with the phosphate phase, the F/P_2O_5 ratio obtained from the bulk analyses is significant. The value of this ratio for all the off-shore phosphorites was 0,14, which is slightly higher than for the Agulhas Bank deposits (0,13) and far greater than the ideal ratio for non-carbonate fluorapatite (0,089) as reported by Rooney and Kerr (1967). This indicates that F is present in excess of the structural requirement for non-carbonate fluorapatite. "Excess" F is commonly reported (Rooney and Kerr, 1967; Gulbrandsen, 1966 and Parker, 1971) and is considered to be introduced to compensate for charge imbalances resulting from the substitution of CO_3^{2-} for PO_4^{3-}. As pointed out by Parker (1971) the relative enrichment of CO_2 in phosphorites from the Agulhas Bank and Cape west coast compared with other localities would necessitate the introduction of additional F into the apatite structure to maintain the charge balance, and hence the abnormally high F/P O ratio is in keeping with the CO_3^{2-}/PO_4^{3-} substitution hypothesis.

A separate investigation involving 41 micro-analyses (including S) of phosphorite cements, phosphate pellets in the matrices and pelletal phosphorites, was instigated in an effort to confirm the coupled substitution of Na^+ and S^{6+}

for Ca^{2+} and P^{5+} suggested by Parker (1975) to explain the co-variance between Na and S noted in the Agulhas Bank phosphorites (Table IV-6).

As can be expected the probe analyses of the matrix showed lower Si, Al, Fe, Mg, K and higher Ca and P values than the bulk determinations. Phosphate pellets which occur in the matrix of some NIII and CI phosphates were found to contain the lowest concentration of diluents and thus these were repeatedly analysed in order to assess the coupled substitution reaction mentioned earlier.

Gulbrandsen (1966) showed that for the phosphorites of the Phosphoria Formation there is an apporximate 1:1 relationship between the atomic ratios of S to Na. He suggests that this is due to a coupled substitution of Na^{+} and S^{6+} for Ca^{2+} and P^{5+}. A similar co-variance was noted by Parker, except that the Agulhas Bank phosphorites show a considerable enrichment of Na over S as regards the 1:1 atomic ratio. Parker suggested that the "excess Na" might have been present in terrigenous feldspar or alternatively that it may represent a substitution of CO_3^{2-}, instead of SO_4^{2-}, for PO_4^{3-} and hence the observed enrichment of Na in relation to S.

Figure IV-12 shows a plot of Na vs S for values obtained from Parker's bulk analyses along with the present micro-analytical data for phosphorite cements, phosphate pellets and pelletal phosphorites. The probe analyses of the phosphorite cements show a similar trend to that of the bulk determinations, exept that the values for Na and S are enriched owing to decreased dilution. The phosphorite pellet data fall closer to the 1:1 substitution line, but do not display the same order of co-variance as do the data from the Phosphoria Formation (Gulbrandsen, 1966). Phosphate pellets from phosphorite No. 2495 and most of the pelletal phosphorite grains are markedly enriched in S and these values plot far above the 1:1 ratio line. X-ray scan images of some of these grains show that part of the S is associated with Fe, indicating the presence of pyrite. However, if all the Fe in the pelletal material is assumed to be associated with the pyrite phase (a reasonable assumption if there is no glauconite (K_2O) present , then the recalculated S values still do not show any co-variance with Na. A similar relationship was noticed by Burnett(1974) in the Peruvian-Chilean phosphorite deposits.

The data is inconclusive mainly because of the presence of "pyritic" S and "glauconitic" Fe. Nevertheless the co-variance between Na and S for the phosphate grains albeit imperfect, adds credence to Parker's original suggestion that a coupled Na^{+} and S^{6+} for Ca^{2+} and P^{5+} substitution is operative in the 4 phosphatic rocks from the Agulhas Bank and Cape west coast. A similar co-variance between Na and S appears to be absent in the pelletal phosphorites.

Table IV-6. Bulk and microprobe analyses of phosphatic material

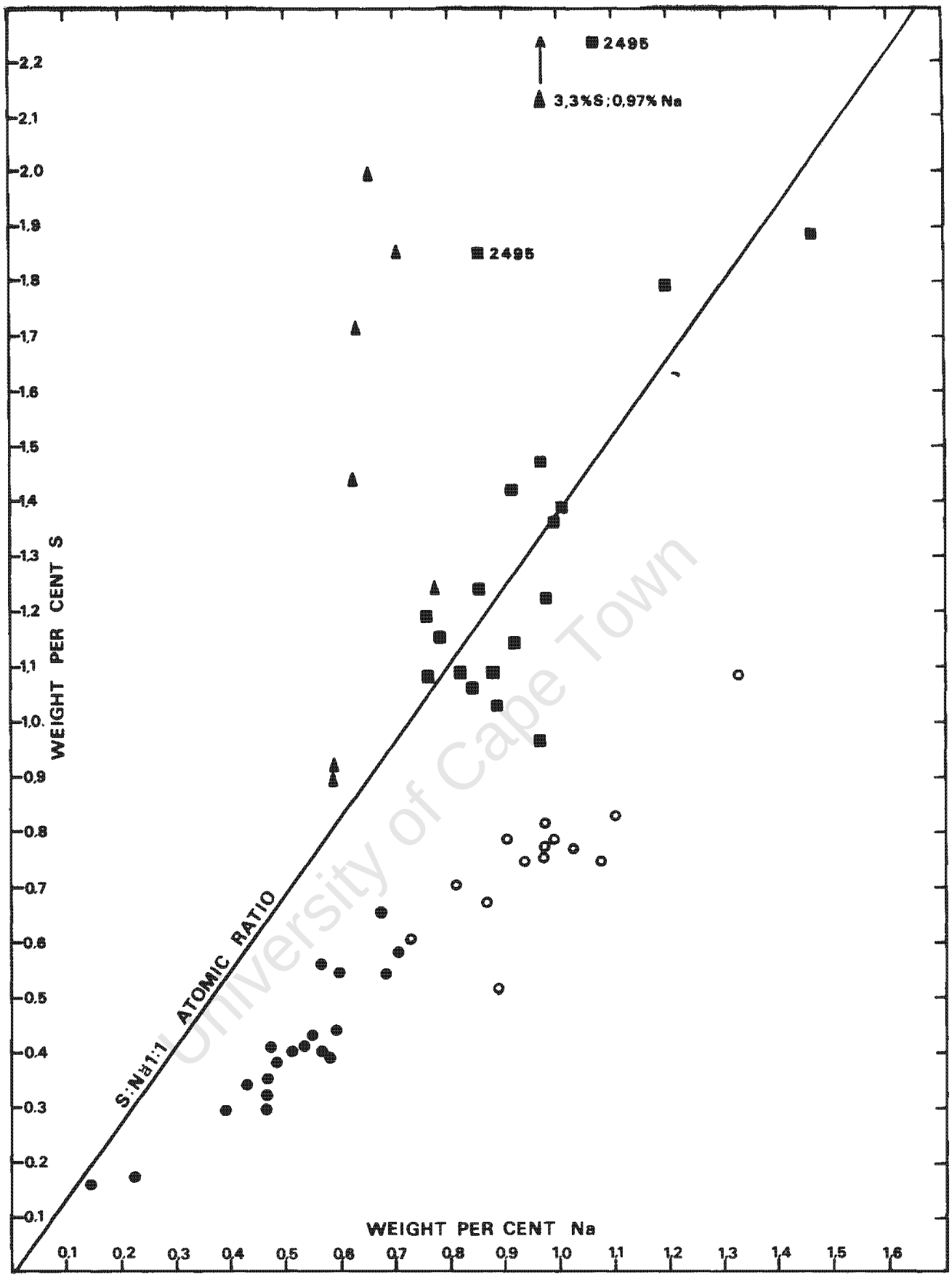
	Phosphorite matrices			Pelletal phosphorites	Phosphate pellets	Phosphorites bulk analyses
	brown matrices from 4.4.9(a)	lime-green matrices from 4.4.9(a)	brown matrices this section			
No. of analyses	10	4	14	8	19	15
SiO_2	7,06	20,18	4,25	4,50	0,19	13,44
Al_2O_3	1,98	2,19	1,53	1,41	0,07	1,70
Fe_2O_3 (1)	1,40	7,79	0,87	1,86	0,93	5,55
MgO	0,81	1,53	0,75	1,04	0,62	1,29
CaO	46,20	34,36	49,32	46,35	50,93	39,27
Na_2O	1,32	0,85	1,38	0,93	1,26	0,98
K_2O	0,51	2,50	0,38	0,43 (2)	0,06	1,19
P_2O_5	28,93	21,58	28,59	29,45	30,66	17,83
S	-	-	0,75	1,67	1,36	0,40 (4)
CaO/P_2O_5	1,60	1,59	1,73	1,57 (3)	1,66	2,20

(1) Total Fe

(2) If the analyses of glauconitized margins are excluded from this mean value, the average K_2O content is 0,25%.

(3) The mean CaO/P_2O_5 value from section 4.6. is 1,38.

(4) From Parker 1971.



WHOLE ROCK AND MICROPROBE ANALYSES
Na vs S

Analyses of Aguilhas Bank phosphorites (Perker 1971) ● whole rock

Microprobe analyses of Cape west coast phosphorites (this work)
- ○ matrix
- ■ phosphate pellets
- ▲ pelletal phosphorites

Figure 1V-12

(d) Ferruginous foraminiferal infillings in the phosphorite matrix.

Foraminifera within the matrix of NI phosphorites from the Childs Bank region (Plate IV-7) are filled with highly ferruginous ($\pm$ 30% Fe_2O_3) glauco-phosphatic material, whereas the ambient matrix contains only minor (0,48% Fe_2O_3) Fe, most of which is associated with the glauconite phase (0,18% K_2O). X-ray scan evidence indicates that the Fe within the test is not associated with S (ie. not pyritic), but is finally disseminated throughout the phosphatic infilling.

The infillings are enriched 50 or 60 times in Fe in relation to the ambient matrix which indicates that the micro-environment within the test acted as a site for preferential precipitation of Fe. The mechanism involved will not be discussed in detail. Phosphate has a tendency to interact with ferric iron, and under favourable low pH conditions, mixed ferric hydroxo-phosphate can be precipitated (Stumm and Morgan, 1970). The point is that phosphate will only become bound with Fe ions under oxic conditions (Manheim et al., 1975). This is in contrast to the anaerobic environment required for apatite precipitation (Burnett, 1974).

4.4.10.Mechanics of glauco-phosphoritic rock formation.

The diagenetic theories postulated by Parker (1971 and 1975) for the genesis of Agulhas Bank phosphorites are in keeping with these new data from the Cape west coast although some of the sedimentary processes are in doubt.

NI and NII phosphorites have formed from foraminiferal lime packstone by the replacement of micrite by collophane through the action of phosphate-rich interstitial solutions moving inwards through partially lithified carbonate rock (Parker, 1971 and Parker and Siesser, 1972).

According to Parker (1971 and 1975) the NIII phosphorites were formed after a transgression when the biogenic depositional zone migrated from the shelf break region across the shelf in response to a rising sea level. Mainly planktonic foraminifera and lime mud were therefore deposited on top of coarser glauconitic and quartzitic mid-shelf sediment. These components were thoroughly mixed by bioturbation and subsequently phosphatized by the same micrite/collophane replacement mechanism as postulated for NI and NII phosphorites.

According to Parker conglomeratic phosphorites from the steeper parts of the Agulhas Bank formed when sediment containing glauconite, quartz and abundant lime mud became unstable and moved down-slope across the outer shelf in the form of a mud flow or turbidity current. During its movement the flow broke up semiconsolidated microfossiliferous sediment (NI phosphorite material), and fragments of this material became incorporated into the turbidite. The poorly-sorted sediment subsequently became phosphatized, forming the conglomeratic phosphorites commonly found near present-day shelf breaks.

A different process must be invoked to explain the presence of conglomeratic phosphorites on the flat, shallow parts of the shelf. Parker (1971, p.60) postulated that currents generated during low stands of the sea carried "muddy glauconitic sediment" across the shelf into the quiet deep-sea environment of the outer shelf on the eastern Agulhas Bank. This mechanism is difficult to envisage as the glauconite deposits on the Agulhas Bank and off the Cape west coast have accumulated as lag deposits through removal of less dense and softer quartzitic and calcitic sediment by wave/current action during transgressive/regressive cycles (Birch, 1971 and 1973). If this sediment were moved great distances (up to 50 n. miles) across flat-lying terrain, one would expect some degree of sorting to have taken place. Instead, these conglomeratic phosphorites are extremely poorly sorted, containing cobbles and pebbles of foraminiferal limestone, silt to coarse sand-size quartz, micrite and delicate foraminifera. Nevertheless, a different mechanism for this admixture of sediment if difficult to envisage. On the flat-lying shelf west of Saldanha Bay both foraminiferal limestone fragments and CI phosphorite have been recovered from the same stations (Nos. 2240 and 2247). This suggests that the two sedimentary types (glauconitic and foraminiferal limestones) formed in different environments at different times. During transgressive and regressive cycles sedimentation zones must have migrated back and forth across the shelf causing overlap of the zones (postulated by Parker for the formation of NIII phosphorites). It is possible that NI phosphorite bedrock, formed during a transgression, may have been broken up by a following regression, and that the new conditions (water depth, change in upwelling etc) prevailing in the course of this period favoured the formation of glauconite. Therefore during the subsequent transgression both the NI phosphorite pebbles and the glauconite were available as allogenic components of the CI phosphorite rock which formed during the following phase of phosphatization. It would thus not be necessary to transport any constituent vast distances over flat-lying topography. This origin would explain the layering observed in some phosphorites and bioturbation could adequately account for the mixed nature of the rock.

4.5. Mixed glauconite/apatite material off the Cape west coast

4.5.1. Introduction.

Glauconite is commonly associated with phosphate deposits (Carozzi, 1958; Emelyanov and Senin, 1969; Rooney and Kerr, 1967 and Summerhayes, 1970) and thus the deposits off the South African coasts are not unique.

High P_2O_5 values in bulk glauconite samples from the Agulhas Bank were originally considered (Birch, 1971) to be due to contamination by fragments of phosphorite rock adhering to glauconite pellets. Later re-examination of these samples revealed a few such composite grains (Plate IV-8), but also

numerous variegated or mottled pellets composed of an intimate mixture of glauconite and apatite. As the investigation proceeded, it became apparent that the glauconite and apatite phases were commonly intimately associated in many different forms, and this aspect of the study became increasingly important.

As a close relationship between the glauconite and phosphate phases has important diagenetic implications and because so little is known about this association (this relationship has only been reported once before; Bailey and Atherton, 1969), it was considered worthy of more detailed study. The X-ray scan, line scan and analytical facilities provided by the electron microprobe proved to be extremely useful tools in the study of these compositional variations as they occur on a microscale.

5.4.2. Microprobe studies on mixed glauconite/phosphate material.

The mixed mineral material has been separated into six types to facilitate description and discussion.

(a) Composite and altered grains.

Composite grains (Plate IV-8) comprising individual glauconite pellets in a phosphorite matrix, and altered pellets have frequently been the cause of contamination of one of the minerals by the other. This type of pellet is easily recognised and accounts for only a very minor proportion of the mixed-mineral material used in this study.

Glauconite grains which have become phosphatized also occur only rarely (note how the phosphate increases regularly towards the outer margin of the grain illustrated in Plate IV-9), but glauconitized pellets (Plate IV-10) are commonly found in the unconsolidated sediment and in the phosphorites. The core of the grain illustrated in Plate IV-10 contains an admixture of glauconite and phosphate, but the glauconite phase becomes increasingly rich towards the outer edge. The grain is coated with a pure phosphatic rim (Parker, 1971). These rims commonly coat such grains and might indicate a rearrangement and extrusion of the phosphate phase from within the pellet as it becomes glauconitized. A similar relocation of phosphate into internal dilation cracks has been observed by Bailey and Atherton (1969). This is discussed later.

(b) Mottled or variegated pellets.

Mottling is most common in the most mature pellets. There is a complete gradation in the scale of mottling, but the pellets have been arbitrarily divided into three groups according to the size of phosphatic segregations.

Light yellow-green areas of randomly intergrown crystallites form segregation of wholly phosphatic material within a dark green purely glauconitic matrix. Coarsely mottled grains (Plate IV-11) have phosphatic segregations between 20 and 50μm in diameter and medium variegated pellets contain a random

distribution of segregations<5μm in size. The finest mottled grains (Plate IV-12) contain an even distribution of individual phosphate and glauconite crystallites <<1μm in size, which even at high magnifications (X2500) are not resolved.

Occasionally mottled grains contain internal dilation cracks (Plate IV-13) which are arranged radially, concentrically or randomly within the pellet. These cracks are usually wholly filled with pure phosphatic material, but occasionally they contain a growth of colourless apatite crystals which radiates normal to the wall of the fracture. Sometimes the surface of the fibrous apatite is in turn coated with orange, Fe-rich ?haematitic material (Bailey and Atherton, 1969). It is evident that these internal cracks have provided sites for recrystallization owing to a rearrangement of the apatite phase within the grain.

(c) Heterogeneous grains.

Heterogeneous grains most commonly consist of a random pattern of predominantly glauconitic or phosphatic material set in a glauco-phosphatic groundmass (Plate IV-14). The patterns are sometimes similar to the matrix of phosphorite rocks or occasionally, the radial patterns resemble replaced biogenic material. These patterns are almost always dissected by the grain edge.

Heterogeneous pellets are markedly different from mottled grains in that neither the glauconitic nor the phosphatic phase is ever pure and because of the distinctly different habits which they exhibit. They also occur in different regions. Mottled grains are most abundant in the large, rich glauconite deposits off the Cape Peninsula and off Saldanha Bay and the heterogeneous grains are almost entirely confined to the mid shelf west of Hondeklip Bay.

(d) Immature phospho-glauconite pellets.

The majority of mixed glauconite/phosphate grains contains a mature (high K_2O) glauconite phase. However, immature pellets have also been found to contain phosphatic material in various forms. Some immature pellets contain phosphatic segregations 5-10μm in diameter and are very similar in appearance to the more mottled varieties described earlier. The immature phospho-glauconite grain presented in Plate IV-15 consists of an evenly distributed admixture of glauconitic and phosphatic material, similar to the finely mottled mature pellets. Note the foraminiferal test enclosed in the grain is filled wholly with glauconite and the calcite shell has remained unaltered.

It is clearly evident from these X-ray scans that the phosphate phase is present at the very earliest stages of pellet formation and that, because of its distribution, it is unlikely that it was formed by phosphatization of the pellet after pellet formation.

(e) Foraminiferal infillings.

Four plates (IV-16 to 19) of foraminiferal infillings are presented; each shows a test which has been filled by a variety of glauconite and phosphorite mixtures by different processes.

Plate IV-16 shows a finely (particle size<1μm) disseminated homogeneous mixture of glauconitic and phosphatic material filling a foraminiferal test. Note that the ambient phosphorite matrix is of a similar composition to the fill material, but that the calcite shell has remained unaltered. The foraminiferal test presented in Plate IV-17 has been filled from the chamber wall for the first $\pm$100μm by fine (<10μm) layers of alternating glauconitic and phosphatic material. Subsequent filling involved an almost wholly apatitic phase ($\pm$100μm thick), followed finally by a further $\pm$50μm of pure glauconite. Note that the secondary test, although partly out of the photograph, shows the same alternating glauconite/phosphate layering and that different parts of the wall of the foraminifera have been altered to glauconite or apatite.

The preceding two examples of foraminiferal infillings are important because they represent two entirely different mechanisms of glauconite and phosphate formation. The uniformly disseminated mixture of glauconite and phosphate represented in Plate IV-16 implies that the particles must have been introduced into the chamber contemporaneously and randomly deposited. The particles may originally either have been clay and calcite crystallites which subsequently altered to glauconite and apatite or they could already have been altered to these minerals prior to their entering the test. The immature nature of the glauconite phase suggests that the material was still in the process of being altered at the time of burial. The similarity in the composition of the ambient phosphorite matrix and the infilling, indicates that the surrounding sediment was formed in a similar manner to that of the material filling the test.

The concentric layering of alternating glauconite and phosphate filling the test represented in Plate IV-17, on the other hand, tends to imply that the layers were formed by the precipitation of elements in solution or the flocculation of colloids in suspension and essentially of one phase at a time. This mechanism is similar to the process which produced the glauconite/phosphate veins occurring in phosphorite rocks described in the previous section.

Plate IV-18 shows a foraminiferal chamber which has been filled on different occasions by two types of material. Initially phospho-glauconite was deposited on the wall of the test furthest from the aperture and during a separate authigenic episode, the foraminifera was filled by a more phosphatic material containing a high proportion of silt-sized quartz. The composition

of the infilling is similar to the ambient matrix, but slightly more phosphatic, but the shell of the foraminifera has remained unaltered.

Plate IV-19 shows an infilled benthic foraminifera. The material filling the chambers of the foraminifera becomes more phosphatic towards the aperture and the last test has a composition similar to the ambient phosphorite matrix.

(f) Altered faecal pellets.

Altered faecal pellets are minor constituents of the unconsolidated sediment and occur mainly on the mid and the outer shelves, especially of Saldanha Bay and the Cape Peninsula.

The composition of altered faecal pellets ranges from purely phosphatic (35,08% P_2O_5) to wholly glauconitic (8,56% K_2O). The two phases are often randomly distributed through the pellets and their chemistry is similar to the mixed mineral grains described in the next section.

4.4.3. The chemical composition of the mixed-mineral material.

The 28 determinations of mixed glauconite/phosphorite grains, infillings and faecal pellets were divided for statistical analysis into two groups depending on their P_2O_5 content (<18% P_2O_5 phospho-glauconite pellets and >18% P_2O_5 glauco-phosphatic grains). The results for each group is given in Appendix IV, but the range in values for both types appears below.

SiO_2	Al_2O_3	Fe_2O_3	K_2O	CaO	MgO	Na_2O	P_2O_5
47,20	5,48	19,13(*)	7,90(*)	51,74	5,01	1,84	31,76
2,33	0,33	1,32	0,27	3,16	0,64	0,02	1,96

(*) excludes oxidized glauco-phosphatic grains.

The most important points brought to light by these analyses are that:-

(1) The mixed mineral material varies between virtually pure glauconite (7,90% K_2O) to highly phosphatic material (31,76% P_2O_5), although the latter never occurs undiluted and is generally more contaminated by glauconite than conversely.

(2) The finely mottled grains and the mixed foraminiferal infillings can have a composition very similar to that of the glauco-phosphatic matrix and parts of the coarse mottled pellets can be composed of purely glauconitic material.

(3) The material initially deposited in the inner chambers of some foraminifera steadily changes, some becoming more phosphatic (5,09% to 30,64% P_2O_5) and others more glauconitic. Other infillings are composed of a finely divided mixture of the two phases.

(4) Grains exhibiting more glauconitic outer margins are the dominant pellet variety. These grains are almost always at least partially encircled by a phosphatic pellicle which, with the exception of the pelletal phosphor-

ites and the phosphate grains, is the only purely phosphatic material present in the unconsolidated sediments and rocks from the Cape west coast. The composition of these grains varies from a core, with a composition very similar to that of the phosphorite matrix ($\pm$3% K_2O; 23% P_2O_5), to a virtually pure glauconitic margin.

The significance of these factors will be enlarged upon in the section dealing with the origin of these authigenic minerals.

The inter-element relationships are almost identical to those already discussed for the phosphorite matrices. All the Ca in the mixed-mineral material can be assigned to the collophane phase, the Mg and Fe are associated with the glauconite, and a very poor correlation between Al and K is similar to that observed in the studies of the pure glauconite phase.

4.6. Off-shore pelletal phosphorite

4.6.1. Introduction

Pelletal phosphorite sediments are discussed separately from the phosphorite rocks because of their distinctly different composition and because they were probably formed by precipitation like the pelletal deposits to the north (Baturin, 1969 and 1972 and Baturin et al., 1970), and not by replacement as are the calcareous phosphatic deposits described in the preceding section.

Pelletal phosphorite has only been found at five sites (<5% of the sand-sized fraction) off the Cape west coast, namely, on the upper slope south of Childs Bank, and south of Cape Point. More extensive pelletal phosphorite deposits occur on the shelf off South West Africa (Summerhayes et al., 1973) and are discussed in detail by Rogers (in prep.(a)) and Bremner (1975(a) and in prep.). The present investigation is restricted to a microprobe study involving 21 analyses and X-ray scans of 31 grains.

The dull resinous brown and reddish-brown pelletal phosphorite occurs as oval or spherical grains predominantly in the medium size fraction. In thin section under plane polarized light the pellets are colourless, but frequently appear mottled by the inclusion of abundant dark organic matter. Although mainly isotropic under crossed nicols, some grains display anisotropic margins, which is thought by Rooney and Kerr (1967) and Tankard (1974(a)) to be due to oxidation during extensive reworking.

4.6.2. Microprobe analyses.

The composition of recent Peruvian-Chilean and South West African phosphorites is presented along with the average composition of 21 pelletal phosphorites from the Cape west coast in Table IV-7. Centre and rim analyses of one pellet are also given in the Table.

Table IV-7. Composition of pelletal phosphorite from the Cape west coast and Recent phosphatic material from South West Africa and Chile-Peru.

	pelletal phosphorite from the Cape west coast				Most apatitic phosphorite matrix analysis from Chile-Peru (1)	Black and brown concretions		Phosphorite matrix.
	average of 12 analyses	range	rim of pellet	centre of pellet		from Chile-Peru (2)	from S.W.A. (3)	
SiO_2	5,51	2,06-17,91	8,04	2,85	2,86	10,80	0,15	7,06
Al_2O_3	1,40	0,54- 2,64	1,85	1,28	1,05	2,55	-	1,98
FeO(4)	4,13	1,08-12,93	2,73	2,67	0,64	2,65	0,18	1,40(8)
MgO	1,10	0,93- 1,26	1,34	0,94	1,10	0,8	-	0,81
CaO	44,90	35,42-53,52	44,05	45,19	46,46	35,01	46,42	46,20
Na_2O	0,84	0,58- 1,21	0,80	1,31	1,27	-	-	1,32
K_2O	0,56(7)	0,16- 1,54	0,93	0,30	-	-	-	0,51
P_2O_5	34,00	26,13-35,94	28,75	28,68	30,45	26,45	32,09	28,93
S	1,67(5)	0,92- 4,73	0,91	3,31	-	-	-	0,75(9)
F	-	-	-	-	2,36	2,45	3,02	-
CaO/P_2O_5	1,320	-	-	-	1,526	1,324	1,447	1,60

(1) Burnett, 1974
(2) Baturin and Petelin, 1972
(3) Baturin, 1969
(4) Total Fe
(5) From section 4.4.9(c) for 10 analyses only
(6) Amorphous Si
(7) If the analyses of the glauconitized margins are excluded from this mean value, the average K_2O content is 0,38%.
(8) Total Fe as Fe_2O_3.
(9) From section 4.4.9.(c).

Pelletal phosphorites are different from the phosphorite rock deposits which are abundant on the Agulhas Bank and off the Cape west coast. They contain no microfossils or biogenic carbonate (low CaO/P_2O_5 values), but they are markedly enriched in apatite (P_2O_5)in relation to the matrix of phosphorite rocks. Pelletal phosphorites contain less Si, Al, Na, Ca and K (if the K-rich grain margins are ignored) and more Fe, and Mg than the most phosphatic matrix variety of the phosphorite rock samples. In relation to Recent phosphorites from South West Africa and Peru-Chile pelletal material from the Cape coast is also greatly enriched in Fe. The pelletal phosphorites from the Cape west coast contain twice the S content of the phosphorite matrix.

An X-ray scan investigation of pelletal phosphorite grains was made to determine the dispersion of the non-apatitic elements. X-ray images of two selected samples are presented in Plates IV-20 and 21 to illustrate the most common dispersion of these elements. Most of the K is disseminated evenly through the grains, but high concentrations often occur in the rims of pellets which have been partially glauconitized (Plate IV-20). This may account for the anisotropic margins observed on some pellets in thin section. The pellets always contain silt-sized quartz grains in varying amounts (up to 9,7% SiO_2). Pelletal phosphorite has an abnormally high S content, some of which (2-3%) is distributed in a mottled fashion throughout the grain. S can also concentrate in the dark core of a pellet or in concentric fractures (Plate IV-20 and 21). Areas rich in S are invariably associated with abundant Fe, indicating the presence of pyrite (d'Anglejan, 1965). A centre-and-rim analysis of one pellet is presented in Table IV-7. These analyses show clearly in quantitative terms the elemental dispersion seen in the X-ray image presented in Plate IV-20, namely an increase in K, Si, Al and Mg towards glauconitized margin of the pellet and high Fe and S values in the pyritic areas nearer the centre of the pellet.

4.7. Onland phosphorites

4.7.1. Introduction.

Comparative studies of adjacent onland and off-shore phosphorite deposits are rare (Summerhayes, 1970) and thus a limited investigation of the onland deposits is warranted, especially as they are considered (Tankard, 1974(a)) to have originated by interstitial precipitation, rather than by replacement as have the adjacent off-shore deposits.

Onland phosphorites are restricted to the coastal lowlands (<200 m) between the Olifants River and Bokpunt (Fig.IV-13), but the largest deposits are near Elands Bay and in the Saldanha Bay region. The phosphorites have formed in a marine environment and occur as massive quartzitic phosphorites and as pelletal phosphorites. They have been studied by Du Toit(1917); Haughton (1933); Visser and Toerien (1971); Visser and Schosch (1973) and Tankard (1974(a) and (b)).

A brief description of the nine sites visited during this investigation is given below.

A small outcrop of friable quartzitic phosphorite is exposed on the hillcrest at Graauwe Duynen (Site 3, Fig.IV-13) and on the seaward side of the hill brown phosphatic pebbles and cobbles are strewn over an extensive area. Occasionally these nodules occur in lenses just below the surface, but in isolated localities phosphorite is exposed along approximately the 100 metre contour line.

Quartzitic phosphorite slabs are exposed intermittently among granite outcrops at Skoongesig. These rocks contain minor pebble inclusions, phosphatized shell and bone and are bored by organisms. Rounded phosphorite pebbles and cobbles composed of the same material are frequently seen in road cuttings below these outcrops and have probably been derived from them. Similar cobbles occur 1 to 3 metres below unconsolidated quartzitic overburden at an altitude of approximately 75 to 100 metres in the region north of Lamberts Bay (Sites 1 and 2). The most economically important phosphatic material at Skoongesig lies in the extensive deposit of pelletal ore in the thick windblown calcareous sands covering the surrounding hills (Site 5).

Quartzitic phosphorite approximately 2 metres thick is poorly exposed at an elevation of about 80 metres on the farm Crywagenskraal near Bokpunt (Site 9). The outcrop can only be followed over short distances and is very similar in appearance to the Varswater deposit which is discussed in more detail.

The only phosphorite presently being exploited comes from an open pit mine on the farm Langberg near Vredendaal. Mining at Varswater Quarry (Site 7) has exposed a rich layer of pelletal phosphorite which is overlain by barren limestone and semi-consolidated quartzitic sand. The phosphate pellets are fine to medium sand-size and are composed of platey skeletal material and spherical or oval grains. The basal Miocene quartzitic phosphorite (Saldanha Formation) is discontinuous and irregular in thickness and no meaningful estimate can be made of its lateral extent. The normally undulating and pitted surface of these rocks can be wind or water polished. Rounded phosphatic cobbles and pebbles occur immediately above the basal quartzitic phosphorite and almost definitely derived from this source. In some localities the basal bed is conglomeratic and even brecciated, and deep hollows in the rock made by boring organisms is additional evidence of a shallow marine origin. The pelletal phosphorite is thought by some (Tankard, 1974(a)) to have originated by disaggregation of the underlying quartzitic phosphorite beds.

The phosphate deposit in the Bomgat cave (Site 6) on the Hoedjiespunt peninsula near Saldanha is unique in that it is not a quartzitic phosphorite.

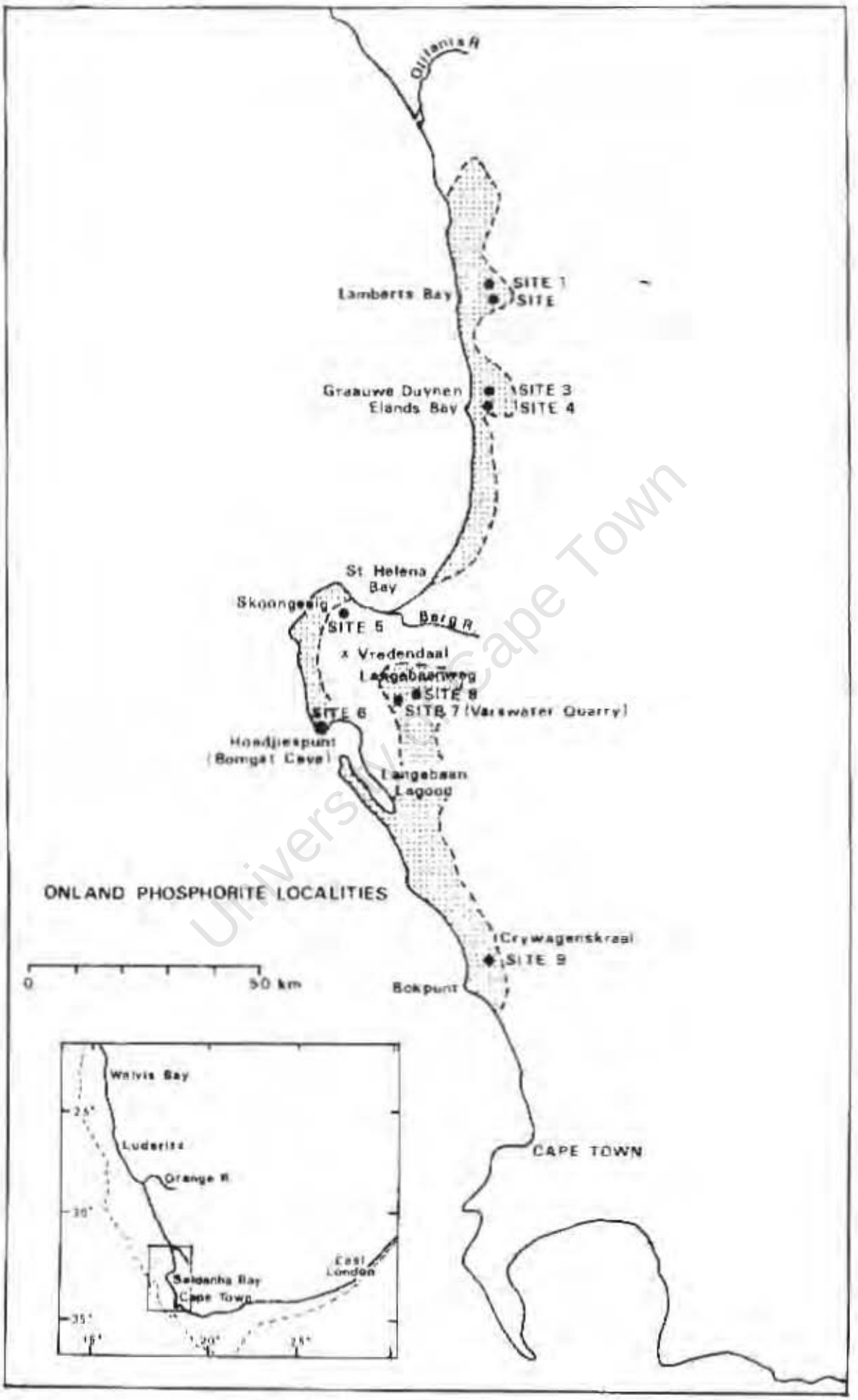

Olifants R
Lamberts Bay
SITE 1
SITE
Graauwe Duynen
Elands Bay
SITE 3
SITE 4
St Helena
Bay
Skoongesig
SITE 5
Berg R
Vredendaal
SITE 8
SITE 6
SITE 7 (Varswater Quarry)
Hoedjiespunt
(Bomgat Cave)
Langebaan
Lagoon
ONLAND PHOSPHORITE LOCALITIES
Crywagenskraal
SITE 9
0
50 km
Bokpunt
Walvis Bay
25°
Luderitz
Orange R
30°
East
London
Saldanha Bay
Cape Town
35°
15°
20°
25°
CAPE TOWN

Figure IV-13

The basal one metre of calcareous sand, shells and skeletal debris has been completely altered into a highly (34-36% P_2O_5) phosphatic resinous rock. The phosphate deposit is immediately overlain by large rounded granite boulders and a further 30 metres of aeolianite.

4.7.2. Petrography.

A petrographic study of 25 thin sections was made of samples from the nine onland sites. Mineralogical abundances were estimated visually using charts provided by Terry and Chilinger (1955), and were checked by making a number of point count analyses, with satisfactory results. A detailed petrographic study of the three phosphorite types has been made by Tankard (1974(a) and (b) and in press) and only a brief description is presented below.

(a) Quartzitic phosphorite.

Quartzitic phosphorite consists essentially of 30-70% fine to medium sand-sized quartz set in a light brown collophane cement. Other constituents include phosphatized bone and shell, minor heavy minerals, mainly ilmenite, and rarely pelletal phosphorite. "Drusy" collophane (Tankard, 1974(a) is present in the phosphorites from Skoongesig and in the Varswater Formation. Finely divided organic and argillaceous material is always present in the cement. The quartzitic phosphorites are termed "medium to fine grained collophane packstones" by Tankard (1974(a)).

(b) Pelletal phosphorite.

Pelletal phosphorite is resinous light- or reddish-brown grains which occur most commonly in the medium sand-size fraction. Oval or spherical grains are structureless, but platey and irregular fragments have obviously been formed by alteration of the bone and skeletal material. According to Tankard (1974(a)), the well-rounded and platey varieties are characteristic of deposition in a littoral environment. The pellets typically contain angular silt-sized quartz grains and a varying amount of organic and argillaceous material. Rarely quartz fragments have acted as nuclei to the pellet. These pellets resemble the off-shore varieties very closely except for the abundant large quartz and bone inclusions.

(c) Phosphatized coquina at Hoedjiespunt.

The Hoedjiespunt phosphorite deposit is unique in its composition for onland phosphorites and in many ways resembles the off-shore varieties.

The brown resinous material is made up of phosphatized shell fragments, bryozoan debris and minor foraminifera set in a light brown collophane cement. Although minor feldspar is present, quartz is almost totally absent. The rock is porous in places and unaltered micrite and also oolitic structures are not uncommon. Tankard (1974(a)) has classified this as a "phosphatized wackestone".

4.7.3. X-ray diffraction studies.

X-ray diffraction analyses of seven onland phosphorite samples were made to identify the dominant minerals present and to determine the mineralogical nature of the apatite phase, including its CO_2 content.

(a) The mineralogy of the phosphate rock.

The equivalent d-spacings of a typical onshore quartzitic phosphorite and the phosphatized coquina are presented in Table IV-2.

The diffraction traces of onshore phosphorites differ from those of the off-shore deposits in the dominant quartz reflections and the absence of calcite. Mixed-layer clays are present in most samples, but illite could only be positively identified in the nodules from Lamberts Bay and the Saldanha Formation and kaolinite occurred only in the quartzitic phosphorite from Graauwe Duynen. Plagioclase and K-feldspar were identified in almost all samples, but the relative proportions present varied markedly and no regional pattern is discernible.

(b) The apatite phase.

The equivalent d-spacings obtained from the X-ray diffraction investigation are similar to values presented by Tankard (1974(b)). He has identified the chief phosphate mineral in the pelletal and quartzitic phosphorites as francolite and that in the phosphatized coquina at Hoedjiespunt as dallhite.

Unfortunately the CO_2 of the apatite could only be determined by X-ray diffraction methods on 4 quartzitic phosphorites owing to diffuse (004) and (410) peaks. The average value of 2,4% CO_2 is only slightly lower than Tankard's (1974(b)) (2,8% CO_2) figure for the Saldanha Formation, but markedly lower than the CO_2 content of the apatite from the off-shore deposits (5,5% CO_2).

4.7.4. Geochemistry.

The main objective of this investigation was to determine the composition of the various types of onland phosphorite (phosphorites, pelletal and phosphatized coquina) and to compare these data with the composition of the adjacent off-shore deposits. Bulk and microprobe analyses were made of the Miocene basal quartzitic phosphorite and of the pelletal phosphorite in the overlying semi-consolidated Varswater Formation to establish their genetic relationship. These microprobe data are compared with the chemistry of the elevated (200-300 m) Skoongesig phosphorites to illuminate any possible genetic inter-relationship between these two widely separated (25 km) deposits.

The bulk composition of various types of onland phosphorites is presented in Table IV-8 along with micro-analyses of phosphorite cements and pelletal inclusions from the Varswater and Skoongesig deposits. The composition of the off-shore phosphorite is included for comparison.

(a) Whole rock determinations.

The results of the six bulk analyses of the quartzitic phosphorites are reasonably similar; the major variation is in the Si content (45-70% SiO_2) which undoubtedly reflects changes in the concentration of the main diluent, quartz, and also in the Al (probably feldspar and/or clay minerals) content which showed a marked enrichment (2-8 times) in the phosphorites from the three northern deposits. The Fe content is reasonably consistent (0,3 to 4,9% Fe_2O_3) and large variations in Ti (0,04 to 0,66% TiO_2), probably reflect a changing heavy mineral (ilmenite) content. The chemical composition of the quartzitic phosphorite and the phosphatized coquina at Hoedjiespunt is very dissimilar. Because of the quartz dilution ($\pm$ 50% SiO_2) in the former, the values should be almost doubled to make the abundance of other elements comparable with that of the Hoedjiespunt deposit. The results indicate that the phosphatized coquina is enriched in Mg, Ca, P and Na and depleted in the lithopile elements (Al and Fe) as compared with the quartzitic phosphorites. The irregular and sometimes low F content of the Hoedjiespunt deposit has been interpreted by Tankard (1974(a)) to indicate the presence of dallhite, a fluorine-poor carbonate apatite, but high (>1%) fluorine values reported more recently by him (Tankard, in press) indicate that francolite is present as well.

The difference in the bulk composition of onshore and off-shore phosphorites is quite striking. If the excessive dilution by quartz in the onland samples is borne in mind, then it is apparent that the onland phosphorites are enriched in elements (Si, Al, Fe) derived from the terrestrial minerals observed in thin section and X-ray diffraction such as feldspars, quartz and clays and off-shore deposits are rich in Mg, K, Ca, Na and F. The Ca in the off-shore phosphorites is associated with the rich biogenic carbonate content clearly seen in the CaO/P_2O_5 ratio and some of the K (see Al_2O_3/K_2O ratios) and Mg would be related to the abundant glauconite on the shelf. The composition of the Hoedjiespunt phosphorite is closer to the off-shore deposits than is that of the quartzitic phosphorite, and only the high quartz (Si) and glauconite (Si, Fe, MgO) contents of the off-shore material differentiates the two deposits.

(b) Microprobe investigations.

The chemical composition of the pellets and cement of the Varswater Formation is similar to that of the cement of the underlying Saldanha Formation quartzitic phosphorite. On the other hand the inclusions in the matrix of the Skoongesig phosphorite are markedly enriched in Si, Al, Fe (8 times) and K with regard to the cement and the composition of this cement also differs greatly from that of the Varswater deposit. These data support Tankard's (1974(a)) contention that the Varswater pellets are derived from the underlying

Table IV-8. Whole rock and probe analyses of onland and off-shore phosphorites

	ONLAND PHOSPHORITE DEPOSITS									OFF-SHORE DEPOSITS	
	Whole rock determinations			Microprobe analyses (this work)						Bulk analyses	Probe analyses
	This work		Tandard 1974(a)	Saldanha Fm.		Varswater Fm.		Skoongesig		This work	
	Qzitic sst.	phosph. coquina	pelletal phos.	cement	pellets	cement	pellets	cement	inclusions	phosph. rock	pelletal phosph.
SiO_2	55,64	4,12	4,13	3,09	11,16	1,56	3,43	6,00	5,54	13,44	5,51
Al_2O_3	3,29	1,51	1,73	0,92	2,05	1,33	1,24	4,94	10,22	1,70	1,40
$FeO^{(2)}$	1,92	0,33	1,77	1,47	0,49	1,31	2,96	1,11	7,31	$5,55^{(3)}$	4,13
MgO	0,17	0,69	0,28	0,37	0,34	0,31	0,66	0,33	0,47	1,29	1,10
CaO	18,21	47,46	46,97	48,59	46,06	49,78	49,02	46,03	33,53	39,27	44,90
Na_2O	0,19	1,02	0,68	0,19	0,55	0,37	0,47	0,14	0,09	0,98	0,84
K_2O	0,26	0,20	0,26	0,21	0,36	0,17	0,34	0,34	0,61	1,19	0,56
P_2O_5	14,49	33,82	33,16	34,75	33,79	36,04	34,36	35,66	31,57	17,83	34,00
F	1,31	1,66	3,44	-	-	-	-	-	-	2,46	-
S	-	-	0,17	-	-	-	-	-	-	$0,40^{(1)}$	1,67
C_{org}	0,26	0,33	-	-	-	-	-	-	-	0,43	-
F/P_2O_5	0,08	0,049	0,104	-	-	-	-	-	-	0,14	-
CaO/P_2O_5	1,140	1,403	1,415	1,398	1,363	1,381	1,426	1,290	1,062	2,230	1,237
Al_2O_3/K_2O	22,570	7,550	6,654	4,380	5,694	7,823	3,647	14,529	16,754	1,980	3,090

(1) Parker, 1971
(2) Total Fe
(3) Fe_2O_3

quartzitic phosphorite, but the composition of the cement and the pebble inclusions in the matrix of Skoongesig phosphorites mitigate against a common origin with the Varswater deposits.

The off-shore pelletal phosphorites are enriched in Fe, Mg, K, Na and S in relation to the pelletal phosphorite in the Varswater Formation as well as the pelletal analyses made by Tankard (1974(a)). In other respects the composition of the two pelletal phosphorite deposits are very similar. The increased Fe and S in the off-shore deposits are associated with the pyritic phase and the higher K content is due to the glauconitized margins of the grains. The high Na and Mg in the off-shore varieties is probably due to increased Ca substitution in the apatite phase (Lehr et al., 1967).

4.7.5. Origin of the onland phosphorite deposits.

The quartzitic phosphorite in the Langeberg region (Sites 7 and 8) was originally believed (Haughton, 1933) to have been formed by selective replacement of calcareous sediment by percolating phosphatic solutions, the source of which was considered to be guano. Truter (1941) thought that the guano dissolved and soaked into the sand to form phosphate cement by interstitial deposition.

Recent investigators have turned away from guano as being the major phosphate source and consider the deposits to have been formed by purely marine processes. Visser and Schoch (1973) do not explain the mechanism for phosphate enrichment, but associate the process with upwelling of nutrient-rich waters along the coast. Tankard (1974(a)) relates the phosphate accumulations to high biological activity and suggests that apatite precipitation is the prime diagenic process.

As Visser and Schoch (1973) so correctly state, guano is unlikely to have played a role in the formation of the quartzitic phosphorites. Present-day guano accumulations on the bottom of the nearby Langebaan Lagoon revealed a total absence of P_2O_5 build up (Birch, 1973). Also, in contrast to Bushinsky's (1969) findings, the fluvial material being supplied to the area is phosphate-poor (see Chapter II). On the other hand, the strong south-east wind prevailing in the summer months blows directly off shore across St. Helena Bay immediately to the north of Saldanha causing upwelling of nutrient-rich bottom water in the inner shelf region (Shannon, 1966; Bang, 1973(a) and De Decker, 1970).

An anomalously rich diatom accumulation in the modern bottom sediment (see Chapter II) in the St. Helena Bay region is evidence of the importance of this locality in terms of biological activity. Sudden mass mortality of the plankton was probably caused as it is today, by a subsidence in the off-shore wind and a subsequent collapse of the upwelling cells (Clowes, 1954 and De Decker, 1970). The basal Miocene quartzitic phosphorites were laid down

at a time when the sea was approximately 55 metres above its present level (Tankard, 1974(a)). Such a rise in sea level would result in a shallow sheltered bay partly enclosed by granite hills in the locality where the quartzitic phosphorite now occurs. This shallow marine environment associated with intense but episodic upwelling and high related biological productivity and mortality would be ideal for the accumulation and decay of vast amounts of phosphorous-rich marine flora and fauna on the bed of the bay. Evidence for this hypothesis is found in the abundant organic matter and presence of opaline silica in the pelletal phosphate, indicating a very similar situation to that of the upwelled inshore waters off South West Africa where present-day interstitial apatite precipitation is operative (Baturin, 1969, 1971 and 1972). Although the meteorologic conditions prevailing in the Miocene need not have been similar to those occurring today, evidence (Tankard, 1974(a)) indicates that this was in fact the case, or alternatively that the environment was even more favourable then to upwelling and high biological productivity than it is now.

The pelletal phosphorites are almost certainly derived from disaggregation of the underlying basal quartzitic phosphorite. Bulk and microprobe analyses indicate that the materials are of similar composition, and detailed size and petrological studies made by Tankard (1974(a)) support this contention.

The chemistry of the phosphatized coquina deposit is entirely different from that of the pelletal quartzitic phosphorites. The differences not only include the Si and Ca contents, but also more significantly, the different F and Ca/P_2O_5 values. Unlike the phosphorites, there is abundant $CaCO_3$ at Hoedjiespunt and an almost total absence of quartz and clay minerals. High CaO/P_2O_5 and the presence of phosphatized shell material (clearly visible in thin section) in these rocks suggest that the dominant phosphatization mechanism is replacement rather than precipitation (Visser and Schoch, 1973).

The more elevated (>100 metres) quartzitic phosphorites at Skoongesig, Graauwe Duynen and Crywagenskraal have probably formed in a similar manner to calcrete by the upward percolation of phosphate-rich water through the unconsolidated sands as has occurred in Florida (Altschuler, 1965). Evaporation at the surface results in apatite being deposited in the interstices of the upper sediment, thereby forming phosphatic sandstones which have been termed "phoscretes" by local geologists (Visser and Schoch, 1973). Although they are petrographically similar to the basal quartzitic phosphorites, high concentrations of Al and/or Fe differentiate them from the former deposit. Moreover, the elevation at which these deposits occur places them beyond the influence of marine processes since the Cretaceous (Tankard, 1975).

4.7.6. A brief comparison of onland and off-shore phosphorite.

The off-shore deposits are characterized by abundant calcite (Ca) and glauconite (K, Mg, Fe) and the onshore varieties are dominated by plentiful quartz (Si). Finer points of difference are the higher Na, F contents of the off-shore phosphorites and the greater Al values of the onland varieties. Structurally the apatite phase (as deduced from X-ray diffraction) is similar, but higher Ca/P_2O_5 and F/P_2O_5 in the off-shore occurrences indicate a chemical difference in the apatite mineral.

Morphologically the deposits are similar. Very distinctive borings by marine animals are common to both deposits and the quartzitic phosphorites tend to be more localized than the off-shore deposits. The large slabs and tabloid-shaped boulders are largely absent from the onland occurrences.

However, the major distinction is genetic. The off-shore phosphorites are considered to be formed by replacement in an open shelf environment and the onland varieties are believed to originate in a restricted shallow water embayment by interstitial precipitation of phosphate in quartzitic sediment.

4.8. Origin of the glauconite and phosphate minerals

4.8.1. Introduction.

Comprehensive reviews of research into the nature, occurrence, mineralogy, geochemistry and formation of both glauconite (Cloud, 1954; Burst, 1958(a) and (b); Hower, 1961; Pratt, 1961; Triplehorn, 1966 and McRae, 1972) and phosphorite (Bushinsky, 1966; Gulbrandsen, 1969; Tooms et al., 1969 and McConnell, 1973) formation have been made and therefore only a brief summary of these views is presented.

(a) Glauconite formation.

Glauconite originates by alteration or replacement of various materials or by precipitation of elements in solution or colloids in suspension.

The materials most commonly reported to have been altered are infillings of foraminifera (Emery, 1960 and Ehlmann et al., 1963); faecal pellets (Takahashi and Yagi, 1929; Takahashi, 1939 and Pratt, 1962(a) and (b); agglomerates of clay-size material (Bailey and Atherton, 1969 and Odin, 1971) and the transformation of biotite (Galliher, 1935(a) and (b), 1936, 1939 and Seed, 1965).

Replacement of calcitic material, often preferentially, is commonly reported (Kharkwal, 1966 and Seed, 1968), but replacement of non-maceous silicates is also frequently described e.g. quartz (Hadding, 1932), feldspar, volcanic glass (Takahashi, 1939), andesite (Hendricks and Ross, 1941) and rhyolite (Ojakangas and Keller, 1964).

Hadding (1932) considers that glauconite impregnation of sponges and

fossil fragments takes place from colloidal suspensions, and Pratt (1962(a)) believes that foraminiferal infillings and encrustations of glauconite are formed by direct precipitation of elements held in solution or colloids in suspension, rather than by replacement. A similar view is held by Bjerkli and Östmo-Saeter (1973), for infillings of Holocene age off the Norwegian coast.

(b) Origin of marine apatite.

Basically two mechanisms have been postulated for the genesis of marine apatites. The one theory favours direct inorganic precipitation of the apatite phase from phosphate-saturated sea water (Kazakov, 1937; Dietz et al., 1942 and McKelvy et al., 1953). The second hypothesis entails the inorganic replacement of previously existing calcitic material by phosphate-rich interstitial solutions to form carbonate fluorapatite (Ames, 1959; Simpson, 1964; Summerhayes, 1967 and 1970 and Parker and Siesser, 1972). Both theories are not only supported by field observations but by experimental and theoretical evidence as well (Simpson, 1964 and Gulbrandsen, 1969).

The controversy concerning the mechanism of phosphorite formation is to some extent due to a lack of thorough investigations of modern marine authigenic processes. Recently studies in the upwelling regions off South West Africa and Chile-Peru (Baturin, 1969; Burnett et al., 1973 and Burnett, 1974) have renewed interest in the important precipitation process. Some of the developments in investigations into the precipitation process since the most recent review of marine apatites (Tooms et al., 1969) warrant further discussion.

The conditions necessary for the precipitation of carbonate apatite from sea water have been found (Gulbrandsen, 1969) to be similar to those which would favour the precipitation of calcium carbonate. But no authigenic calcium carbonate formation has been observed in anaerobic sediment and in fact calcium carbonate appears to decrease with depth in highly phosphatic pore waters (Brooks et al., 1968). Berner et al. (1970) have shown that calcium carbonate can be super-saturated in pore waters without precipitating owing to the inhibiting effect of dissolved organic matter. This has led Burnett (1974) to believe that the ubiquitous presence of vast amounts of organic matter in the sediments from the highly productive upwelling regions off Peru-Chile is sufficient to act as an inhibiting agent to calcium carbonate deposition.

A further problem in the precipitation of apatite in marine sediments has been revealed by the experimental work of Bachra et al. (1965) and Martens and Harriss (1970) who have shown that the presence of Mg^{2+} ions also inhibits the precipitation of apatite, probably because Mg^{2+} ions compete with Ca^{2+} sites in the apatite structure. However, the work of Martens and

Harriss (1970) also predicted that there was probably a threshold of $^{Ca}/_{Mg}$ above which apatites could precipitate. Burnett (1974) and Atlas (1975) have proposed that the $^{Ca}/_{Mg}$ ratio could be increased in the pore waters of organic sediment by certain diagenetic reactions or a combination of reactions such as Mg^{2+} replacing Fe^{3+} in clays, dolomitization or authigenic formation of Mg-rich silicates e.g. nontronite, sepiolite or chlorite. Baturin (1972, p.854) favours the presence of carbonate material which acts as an "ion exchanger, driving the Ca out of the solution and removing the Mg".

Burnett (1974) has proposed the following model to account for the apatite which is presently precipitating out of anoxic pore waters in diatomaceous oozes on the Chile-Peru shelf. Upwelling of nutrient-rich water and high biological activity provides a large input of organic matter to the shelf sediments. During periods of increased average sea water temperatures apatite precipitation is initiated by high PO_4^{3-} contents in the pore waters. The inhibiting effect of Mg^{2+} ions is removed by diagenetic reactions in such a way as to increase the $^{Ca}/_{Mg}$ ratio above the threshold for apatite to precipitate. Particles of organic debris frequently act as nucleation sites in the initial stages of precipitation. Thereafter, the reaction may be self-perpetuating as long as there is a continuous influx of phosphate into the system.

4.8.2. Glauconite and phosphorite formation off the Cape west coast.

Authigenic deposits on the continental margin off the Cape west coast vary from purely glauconitic to wholly phosphatic material, but these deposits are rare, and by far the most common authigenic material is composed of a mixture of these two minerals.

The onland quartzitic phosphorites and the off-shore pelletal phosphorites will be discussed first and the off-shore glauco-phosphorites will be dealt with next. The origin of the glauconitic materials is discussed last.

(a) Phosphorites.

The onland pelletal and quartzitic phosphorites are included in this discussion because they are believed to have been formed under marine conditions during the same period as the off-shore deposits and therefore they should be regarded as part of the continental margin as far as this investigation is concerned. These deposits are believed (Tankard, 1974(a) and (b)) to have originated in shallow marine conditions by precipitation in areas of intense upwelling and high biological productivity. The phosphates which are concentrated from the sea water by organisms, are liberated in the bottom sediment during organic decay. Carbonate apatite is precipitated within the pore waters of the sediment by the same mechanism as that proposed by Burnett

(1974). These deposits are analogous to the phosphorites off South West Africa and have probably formed in a similar manner to those forming in the highly organic diatomaceous muds off that coast today (Baturin, 1969). There apatite is precipitating along the edge of the diatomaceous mud belt at the interface between the oxidizing and reducing environment (Senin, 1970), probably owing to a change in the pH (Burnett, 1974). The associated onshore pelletal phosphorites are probably formed by disaggregation of the underlying quartzitic phosphorites during transgressive/regressive periods or by marine agents through tectonic changes in a similar manner to that envisaged for the formation of the ancient mid-shelf pelletal deposits off South West Africa (Senin, 1970).

Minor, isolated occurrences of pelletal phosphorite occurring near the shelf break south of the Childs Bank and west of Danger Point are very similar to the more extensive pelletal deposits off South West Africa. A phosphorite (Plate IV-4), closely resembling one recovered from the Chilean-Peruvian shelf ($\pm$ 375 metres), has been trawled by a commercial fishing vessel from the outer shelf south of Cape Point in roughly the same vicinity where the pelletal phosphorite has been found (unfortunately the exact locality is unknown). This rock is characterized by the total absence of carbonate detritus. It contains approximately 40% fine sand-sized quartz and minor (<1%) fragmented glauconite set in a light brown collophane cement. It is thus very unlike the glauco-phosphorite rocks from the Agulhas Bank and elsewhere off the Cape west coast.

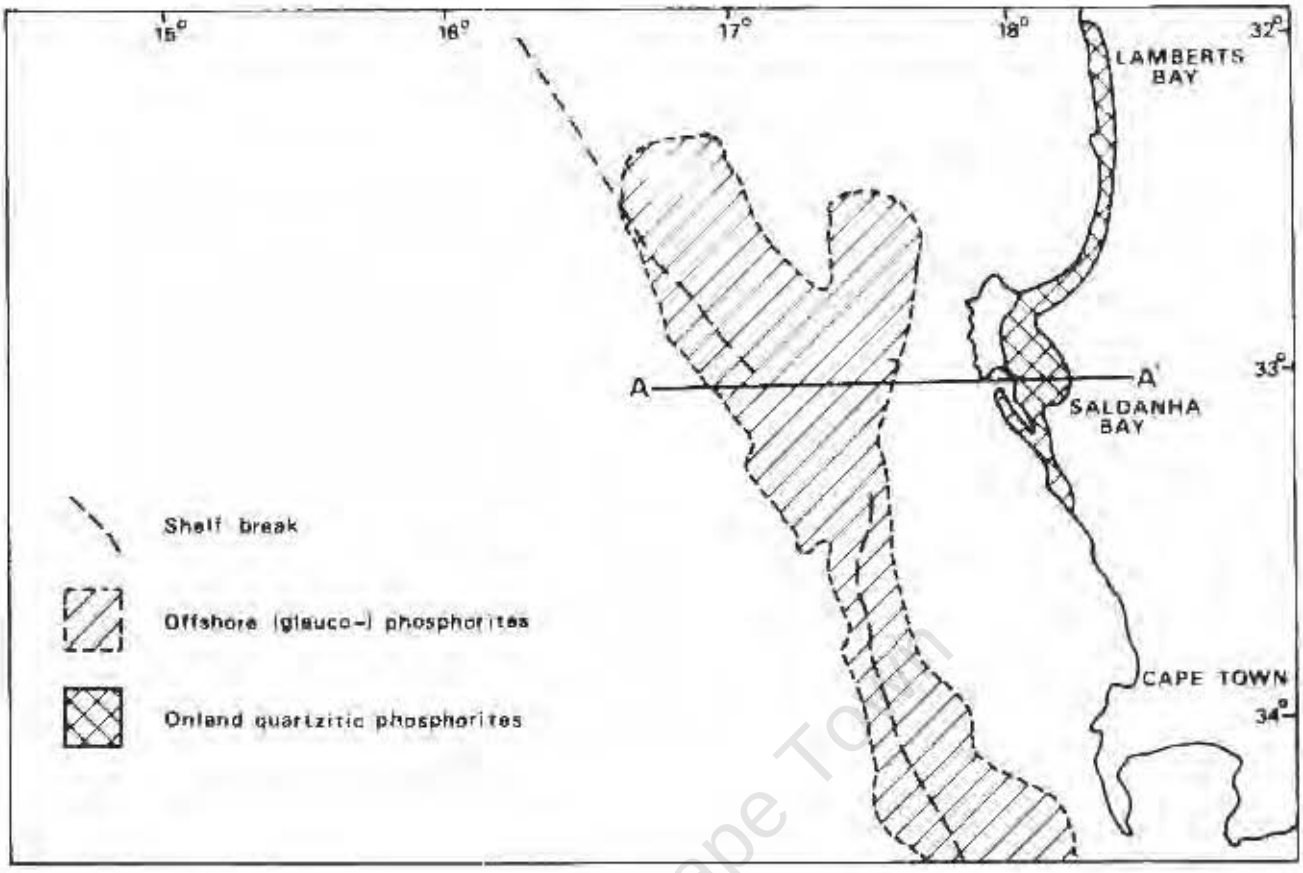
These occurrences suggest that the rich pelletal phosphorite deposits off South West Africa were once more extensive and may have extended along the outer shelf as far south as Danger Point.

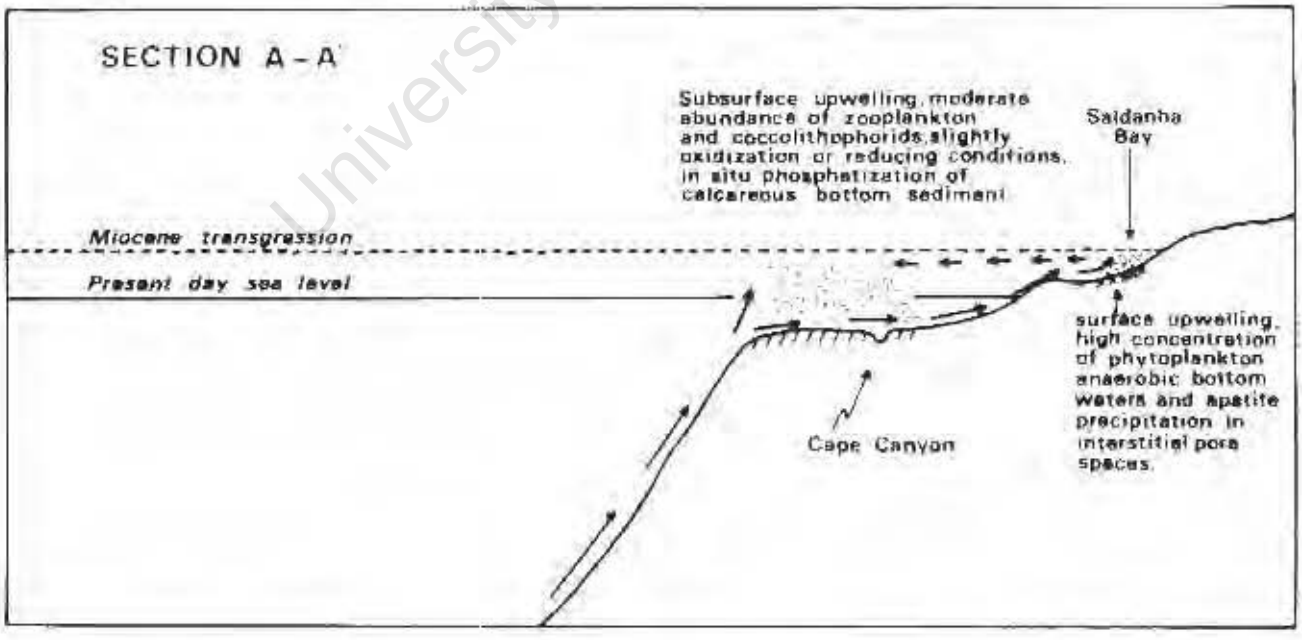
The extensive deposits of phosphatic rocks covering vast areas of the Agulhas Bank and the Cape west coast are considered (Parker, 1971 and Parker and Siesser, 1972) to have been formed by replacement of calcitic material, mainly calcareous mud (micrite). These deposits are contrasted with the more localized nearshore pelletal and quartzitic phosphorite deposits occurring in the regions of intense upwelling which have originated by precipitation (Tankard, 1974(a)). Sudden blooms of siliceous phytoplankton are common in the nearshore upwelling regions and the bottom sediment in these areas tends to be highly organic, anaerobic and devoid of calcareous material. Holocene foraminifera found in the anaerobic sediments off Peru by Manhein et al. (1975) were possibly deposited during intermittent slackening in upwelling and only became phosphatized later, after resumption of normal organic accumulations and anoxic conditions. More diffuse and less intense upwelling associated with the zone of divergence on the mid and the outer shelves results in a lower nutrient contribution to the water mass and thus biological

activity is less than in the nearshore regions (Fig.IV-14). Nevertheless, it appears that the death of considerable quantities of mainly calcareous zooplankton living in these waters may have contributed sufficient phosphate to the bottom sediment to cause phosphatization of micrite in the past.

A major difference between the nearshore phosphatic deposits and the open shelf phosphorites lies in the composition of the cementing medium. The ubiquitous presence of finely divided glauconite in the cement of the latter deposits is not paralleled in the quartzitic and pelletal phosphorites. The maximum K_2O content of the pelletal material is <0,5% (excluding those samples where the outer margin of the pellet has been glauconitized subsequent to the formation of the pellet), whereas the cement of the open shelf phosphorite rocks contains between 0,5 and 3% K_2O. The origin of this mixed material could be simply explained by the glauconitization of previously existing phosphatic material. The existence of finely divided (<1μm) glauconitic particles evenly disseminated through the phosphatic cement is difficult to comprehend in terms of this supposition. It is highly improbable that submicron-sized particles within the matrix of a phosphorite deposit could become selectively glauconitized without affecting the ambient matrix. The outer surface of some rocks has been glauconitized and in these examples an alteration gradient is clearly visible. The same feature has been observed on the outer surfaces of NI phosphorite rocks which have been phosphatized (Parker, 1971), but these features should not be confused with the homogeneous mixture of glauconite and phosphate comprising the matrix of the off-shore phosphorites.

An alternative explanation for this small but significant glauconite component in the phosphorite cement follows. The sediment on the mid and the outer shelves is mainly a mixture of micrite fine quartz and clay minerals, but because phosphorite formation requires a negligible influx of terrigenous sediments (Pevear, 1966 and 1967), carbonate deposition can be expected to be dominant as it is in these regions today. The accumulation of organisms on the sea floor may provide sufficient P and Fe to cause phosphatization of the calcareous mud and also to convert the clay minerals to glauconite contemporaneously. This theory would adequately account for the formation of the mixed mineral foraminiferal infillings and the heterogeneous glauconite/apatite grains from the phosphorite region south of the Childs Bank. The small (<100μm) pockets of more glauconitic material between grains within the cement of some phosphorite rocks (Plate IV-5) could then be explained by the preferential accumulation of clay particles which were subsequently glauconitized.





MODEL OF PHOSPHATE PRECIPITATION AND REPLACEMENT

Figure IV-14

(b) Glauconites

Morphological, mineralogical and geochemical investigations of glauconite have revealed several features which require explanation in terms of diagenetic processes. These are: the formation of the glauconite pellet itself; the origin of mixed glauconite/apatite grains; and the source of the Fe required by the glauconite structure.

Although there is ample evidence off the South African coasts for both alteration and precipitation mechanisms, the size, morphology and distribution of the majority of glauconite grains exclude the possibility of their forming by alteration of faecal pellets or foraminiferal infillings or by replacement of any non-clay detrital mineral e.g. feldspar, pyroxenes etc. Although the origin of the glauconite pellets remains problematical, two theories are presented which take into account some of the diverse requirements for their formation.

Glauconite and phosphorite are frequently associated (Hutton and Seelye, 1941; Carozzi, 1958; Rooney and Kerr, 1967; D'Anglejan, 1965 and 1968 and Burnett, 1974), but mottled or variegated pellets containing an intimate admixture of these two minerals have only been reported once previously (D'Anglejan, 1968 mentions apatite within a glauconitized foraminiferal test). Bailey and Atherton (1969) concluded that the variegated glauconite pellets occurring in sandy chalk from Northern Ireland were formed by accretion of colloidal glauconite and phosphate particles. They suggest that ferruginous clay colloids and colloidal phosphate preferentially flocculate in the intergranular, slightly reducing micro-environment of the uppermost sediment layer. Colloidal aggregation continues until the combined mass is sufficient for the pellet to settle out of the water layer immediately above the sediment. Further colloids would be preferentially attracted to the surface of the proto-glauconite/apatite pellet by ionic charge imbalances associated with the particles comprising the pellet, while non-colloidal material remains in suspension. Pellet growth ceases when colloidal attraction and bonding is insufficient to prevent dislodgement of colloidal particles from the pellet surface during agitation, or when burial prevents further colloid movement. Subsequent collapse of expandable layers and enrichment in K would proceed according to Burst's (1958(a)) or Forster's (1969) model of glauconitization. This theory, although attractive, especially in explaining mixed mineral grains, has not been readily accepted, mainly because such colloidal particles have never been observed and because the behaviour of colloidal matter in saline waters is poorly known. The inclusion of qaurtz and shell debris in South African glauconites also mitigates against colloidal aggregation.

There is possibly evidence for an alternative origin for the mixed mineral pellets. It has previously been mentioned that the matrix of some phosphorite rocks contains a significant glauconite component (>3% K_2O) and fragmentation of this sediment has undoubtedly produced the heterogeneous variety of mixed mineral grains (Plate IV-14) found in the ambient unconsolidated sediment. These heterogeneous grains have a similar composition to that of the local phosphorites and the irregular patterns of glauconitic and apatitic material within the pellets are abruptly truncated at the grain surface indicating that the pellet represents a fragment of larger rock.

Although it is evident that the heterogeneous pellets originate by fragmentation of local phosphorite rocks, the origin of the mottled or variegated pellets is not as clear. Their formation could be simply explained by phosphatization of glauconite grains while in the unconsolidated sediment or during their incorporation into a phosphorite rock. However, pellets exhibiting phosphatized margins are rare and pellets with random mottling are common. Furthermore, foraminiferal tests frequently containing an intimate mixture of finely divided (<1μm) glauconite and apatite minerals and also pellets commonly showing marked glauconite enrichment towards the grain surface, are features which are difficult to comprehend in terms of a phosphatization mechanism. The interior of the glauconitized pellets has a composition (3,2% K_2O; 23,3% P_2O_5) similar to that of the glauco-phosphatic matrix of some phosphorites, and the outer margin of these grains are composed of mature glauconitic material (8,6% K_2O; 2,00% P_2O_5). It is feasible therefore, that particles of calcium carbonate and clay minerals in the bottom sediment could be contemporaneously phosphatized and glauconitized respectively as postulated earlier for the phosphorite matrix, and that during a subsequent transgressive/regressive cycle this partially consolidated glauco-phosphatic bedrock could be disaggregated and reworked by wave action. The fragments are then exposed to K-rich sea water and may become rounded and further glauconitized. Summerhayes (1970) has described a similar feature occurring in the sediments off Morocco where reddish-brown ferruginous mudstone fragments, 1 to 2 phi in size, are being altered to glauconite. This would explain the frequent occurrence of pellets exhibiting glauconitized margins as well as the re-organization of the apatite within the grain (Plate IV-22). It might also account for the association of glauconite formation with unconformities, ie. periods of transgression and regression (McRae, 1972), as well as the well-sorted nature of these deposits (Bailey and Atherton are intrigued by the restricted size range of the glauconite pellets). Some "glauconite" pellets containing quartz grains, residual calcium carbonate and foraminiferal tests (Plate IV-22) have almost certainly

originated by the break-up of the bottom sediment, but the relative importance of this mode of formation remains an open question.

The nearshore non-phosphatic glauconite pellets off Hondeklip Bay are large (frequently over 1 mm) and deeply sutured or lobate. These pellets, like the nearshore non-phosphatic glauconite deposits on the Agulhas Bank, overlie argillaceous Cretaceous sediment and are probably derived from them. Because of their size, morphology and internal composition, these pellets could only have been formed by the aggregation of colloidal clay particles or by the disaggregation and glauconitization of clay-rich bottom sediment, as previously described. Several features regarding the pellets are diagenetically significant. Non-phosphatic glauconites, like those nearshore deposits from the Agulhas Bank, are probably derived from argillaceous sediments containing a negligible calcium carbonate content, whereas the most phosphatic glauconites occur on the open shelf where calcareous mud is relatively abundant. This relationship could indicate that there may have been contemporaneous alteration of the calcite and clay minerals in the bottom sediment or alternatively it could support a mechanism of co-precipitation of glauconite and apatite colloids. At least some grains have become glauconitized subsequent to the development of the pellet form (Fig. IV-4), indicating that alteration may have been the most likely process.

It has often been reported (Hower, 1961) that glauconite from sediments with a high influx of detritus (e.g. argillaceous deposits) frequently contains less mature grains than pellets from clean quartzitic or calcareous sediments. This is because glauconite forms at the water/sediment interface and rapid sedimentation arrests the diagenetic process by burial. However, if degraded clay minerals are the precursor of the glauconite mineral, then the sediment in the glauconite-rich areas (some areas contain over 90% glauconite grains by weight) must have been dominantly clay material at the time of formation. This suggests that glauconite formation may in fact take place in slowly accumulating clay-rich sediments and that the main diagenetic phase occurred during a later regression or transgression when the muddy bottom sediment was broken up and further glauconitized.

The most difficult contribution to evaluate in terms of glauconite formation is Fe (Burst, 1958(b) and Ehlmann et al., 1963). The most immature glauconite is highly ferruginous indicating that the Fe must be present either in the original starting material (e.g. biotite), or it must be adsorbed much more rapidly than K (Ehlmann et al., 1963; Seed, 1965 and Porrenga, 1966). Mg and K are also essential constituents of the glauconite mineral, but these elements are far more abundant in sea water than Fe and are probably readily adsorbed by the clay once the glauconitization process is under way (Hendricks and Ross, 1941).

The Fe^{2+}/Fe^{3+} ratio may indicate a semi-oxidizing, semi-reducing environment of formation (Burst, 1958(b)). Most of the Fe in the glauconite structure is in the ferric form which has led Seed (1965) to suggest that it originated as colloidal hydroxide. The consistent Fe^{2+}/Fe^{3+} ratio is possibly not only due to environmental factors, but may also reflect requirements of the glauconite structure (Hendricks and Ross, 1941). The most commonly suggested (Burst, 1958(b) and Pantin, 1966) source for the Fe is by the incorporation into the sediment of large quantities of marine microfauna which have become greatly enriched (between 500 000 and 50 000 times, Chester, 1965 and Martin and Knauer, 1973) in Fe by consumption of ferruginous particulate matter in the sea water (organo-iron complexes and iron-rich colloids). This process is generally thought to occur in areas of upwelling and high biological activity (Burst, 1958(b)). However, the Fe and K content of the <2µm fraction in the areas of intense upwelling and in the relict glauconite deposits has been found to be relatively low (<8% Fe_2O_3, on a calcium carbonate-free basis). In fact, studies (Rogers, in prep.(a), and Bremner, in prep.) now being carried out in the regions of maximum present-day upwelling off South West Africa confirm that the distribution of Fe (and K) along virtually the entire west coast south of the Kunene is related to terrestrial influx and not to biogenous processes. An anomalously high Fe concentration on the outer shelf off Sylvia Hill is as yet unexplained (Rogers, pers.comm.). Nevertheless the highest Fe value there is less than 10% Fe_2O_3. Furthermore, although present-day phosphate formation has been found (Baturin, 1969; Baturin and Petelin, 1972 and Burnett, 1974) in the upwelled regions off Peru-Chile and South West Africa, no reports of modern glauconite diagenesis in these areas have been received. It has recently been found (Drever, 1971) that Fe is actually extracted from clay minerals in anaerobic marine sediments. Mg from the surrounding sea water then replaces the extracted Fe in the clay structure, thereby creating an environment favouring the precipitation of apatite (see phosphorite section) rather than the formation of glauconite. Orren (1969) has also found that the Fe content of sea water in the upwelled waters off South West Africa is depleted near the bottom and most abundant above the thermocline in mid water, indicating that Fe is being recycled back into the sea water. Perhaps Fe is also unstable in these anaerobic bottom sediments because it is in the more soluble ferrous state and because it is only precipitated in the less soluble ferric Fe form in the more oxygenated adjacent areas (Torr, 1920; in Burst, 1958(b)). Reworked pelletal phosphorites, which are believed to have been formed by precipitation in anaerobic conditions, frequently have glauconitized margins, thus indicating that Fe (and K) is available in the sea water once outside the reducing environment. This could also explain the divergent but parallel

distribution of maximum phosphate and glauconite occurrence which is apparent in most regions off the South African coasts (Birch, 1973 and Rogers, 1973).

Although glauconite could not form within anaerobic sediment because of competition with the sulphide phase, Fe is clearly available on occasions in regions of less intense upwelling in the oxygenated bottom waters of the open shelf. This is evident from the glauconite solutions permeating through the phosphorite rocks; the highly ferruginous phosphatic infillings and the glauconitized margins of mixed mineral grains. Moreover, the distribution of relict glauconite on the south west coast of Africa (Rogers, 1973 and Bremner, 1975) is clearly related in some manner to areas of low terrigenous sedimentation and to regions of upwelling (e.g. off the Cape Peninsula and west of Saldanha Bay). It is also unlikely that the Fe is derived directly from a terrestrial source alone, as the Fe content of the <2μm material presently being introduced in the marine environment is less than 10% Fe_2O_3.

A correlation between the Fe content of glauconite and the age of formation has been found by Smulikowski (1954), who suggests that the sea bottom has become enriched in Fe and depleted in K. But more recent work by Bentor and Kastner (1965) has revealed no correlation between age and glauconite composition. There is evidence (Burst, 1958(b)) that the formation of the most highly ordered glauconite (ie. rich in Fe and K) is associated with unconformities. Although sedimentation rates on the mid and the outer shelves are low at present there is no indication of glauconite (or phosphorite, Baturin and Dubinchuk, 1974) formation which would indicate that the elements needed for the formation of these minerals are not being supplied to the sea floor, or alternatively that they are not being retained there. It appears that the physico-chemical conditions necessary for the retention of these elements in the sediment, occur mainly during transgressive/regressive periods, possibly because of increased upwelling and faster accumulation of K- and P-enriched organisms on the sea floor or possibly because of collapse of the recycling system presently operative in the water column.

4.9. Ages of phosphorite and glauconite formation and the economic potential of these deposits.

4.9.1. Ages of glauconite and phosphorite formation.

The ages of phosphorite formation have been determined mainly by association with other rock types (Siesser, 1972; Dingle, 1971, 1973(b) and Parker and Siesser, 1972). Stratigraphical relationships have led Dingle (in press) to postulate two main phases of Tertiary phosphatization associated with regressive sea level movements, namely Upper Eocene and late Miocene/early Plio-

cene or late Pliocene. The later period correlates well with a fossil determination made by Haughton (1956). The onland quartzitic phosphorites have also been dated as Miocene, but they have formed during a transgressive period (Tankard, 1974(a)). Transgressive phosphatization is also suggested by the frequent occurrence of phosphatized foraminiferal lime packstone (NIA phosphorites, see section 4.4.) on the inner shelf in regions of present-day terrestrial deposition.

Since Dingle's (in press) review article, six NI phosphorites have been dated, three on nannofossil evidence by Siesser (1975) and the remainder on foraminiferal assemblages by Dr. D. Bayliss (pers.comm.). The sample numbers, age and depth are recorded below.

Station	Maximum age range	Probable age	Depth(m)	Fauna
1706	M.Miocene - U.Miocene	M.Miocene	305	Nannofossils
2246	M.Eocene - U.Miocene	M.-U.Eocene	315	Nannofossils
2361	-	M.Miocene	241	Foraminifera
2449	M.Eocene - U.Miocene	M.Miocene	388	Nannofossils
2984*	-	M.Miocene	250	Foraminifera
2922*	late Eocene to Miocene	M.Miocene	190	Foraminifera

* Rogers, 1974

Although the Nummulitic limestone (2361) was recovered from the quiet water, outer shelf region west of Hondeklip Bay, its faunal assemblage suggests that it was originally deposited in an outer sublittoral environment. The M. Miocene age is indicated mainly by the presence of keeled globorotalids of the G. fohsi group. Two similar Nummulitic limestones recovered off the Orange River have been assigned a M. Miocene and a late Eocene to Miocene age by Dr. Bayliss (Rogers, 1974).

Five of the phosphorites were dated as probably L. or M. Miocene, which may indicate a refinement of Dingle's late Miocene/early or late Pliocene period of phosphatization and a probable M. to U. Eocene age for the phosphorite from station 2246 correlates well with Dingle's earlier phase of phosphatization. No recent phosphate diagenesis is evident, a feature supported by uranium isotope investigations (Kolodny and Kaplan, 1970) and recent electron microscope evidence (Baturin and Dubinchuk, 1974).

A Miocene-Pliocene period of phosphatization has also been suggested by other workers (Kolodny and Kaplan, 1970 and Tooms et al., 1969) studying worldwide occurrences of phosphorites. Important features in the formation of phosphorites are upwelling and high sea water temperatures, and Kolodny and Kaplan (1970) suggest that this period of phosphatization is associated with higher temperatures during the Miocene compared to Recent times (Tooms et al., 1969). Sea water is at present saturated or super-saturated with regard to apatite and since the solubility of apatite decreases with increas-

ing temperature a change in temperature may be sufficient to cause phosphorite formation. Valuable new evidence concerning upwelling along the west coast of Africa has recently become available. It appears that it is only since the Early Oligocene that the South Atlantic Ocean has developed sufficient width to allow the climatic and oceanic systems of the southern Atlantic to be established along the west coast of Africa (Zinderen Bakker, in press). Moreover, the Tasman/Ross shelf shear zone only parted in the mid Tertiary and it is only in the Early Miocene times that Australia had drifted far enough away from Antarctica for a continuous route to form so that the cold circumantarctic current in the Southern Ocean could develop (Kennett, 1973). It thus appears that it is only since the Miocene that upwelling commenced along the west African coast and this, combined with the reported increase in temperature, introduced sufficient phosphorous into the bottom sediment to cause widespread phosphatization.

Glauconite on the continental margin surrounding South Africa is probably all eroded from underlying, mostly Tertiary phosphorites and limestones (Birch, 1971).

Three glauconite samples from the rich deposit off the Cape Peninsula have been dated by Dr. I. McDougall (The Australian National University) by the K/Ar method as M. Miocene to L. Pliocene.

Station	Age	Range
110	L. Pliocene	$6,50 \pm 0,12$
112	U. Miocene	$8,57 \pm 0,13$
286	M. Miocene	$17,7 \pm 0,2$
foraminiferal* infillings	M. Miocene	$15,0 \pm 0,3$

* sample was concentrated from sediment from stations 1706, 1700 and 1699.

It is interesting to note that the L. Pliocene glauconites from station 110 occur adjacent to the non-glauconitic NI phosphorite (1706) which was dated by Dr. Siesser as M. Miocene and that conglomeratic CI phosphorites from the same station contain similar NI phosphorite pebbles and abundant glauconite. This glauconite is very similar to that in the ambient sediment and to that which was dated by Dr. McDougall. If the enclosed NI phosphorite pebbles can be equated with the ambient M. Miocene NI phosphorites and if it is assumed that the glauconite in the unconsolidated sediment is derived from the surrounding CI phosphorites, then the authigenic history for this area can be reconstructed thus: Foraminiferal lime mud was phosphatized in the M. Miocene and this was followed in the early Pliocene by extensive glauconitization. Reworking of this sediment caused rounding of the glauconite pellets and partial disaggregation of the phosphatized non-

glauconitic limestone. These deposits subsequently became phosphatized during a later authigenic episode. More recent erosion has released some of the glauconite from the matrix of the CI phosphorite to the overlying unconsolidated sediment.

A glauconite sample composed of "fresh" clay-like glauconite still within foraminifera and slightly darker green glauconite partially free of the foraminiferal test, was also sent for dating to substantiate that these glauconites did not represent recent glauconite diagenesis. However, these infillings also proved to be M. Miocene in age, thereby refuting an earlier suggestion (Birch, 1971) that minor present-day glauconite formation was occurring off the Cape Peninsula.

4.9.2. The economic potential of the glauconite and phosphate deposits.

Assuming that all the exposed rock on the mid and the outer shelves shown in Figure I-2 contains at least 5% P_2O_5, and that it is 0,5 metres thick, then the rock phosphate constitutes a reserve of at least 880 x 10^6 metric tons P_2O_5, whereas, if only the sediment containing in excess of 4% P_2O_5 is considered, the top 0,5 metres of phosphatic sand are calculated to contain at least 300 x 10^6 metric tons P_2O_5. If the sediment composed of greater than 60% glauconite is 0,5 metres thick, then the deposit constitutes a reserve of at least 425 x 10^6 metric tons K_2O.

Rogers et al. (1972) and Granville (1974) have recently assessed the economic potential of the glauconite and the phosphatic deposits off the South African continental margin. Parker (1971) reports that pot-plant tests have shown that the availability of phosphate from the unrefined, and low grade phosphorites is comparable to that of superphosphate. However, Granville (1974) concluded that as there was a plentiful supply of high grade (31-36% P_2O_5) land-derived phosphate and because of the difficulties of marine mining, the potential of these deposits was highly problematical.

Although the world supplies of potash are adequate, South Africa is dependent on imports for her supplies. Glauconite would be easily beneficiated by screening and large concentrations occur close to major ports. Granville therefore suggests that consideration should be given to the glauconite deposits for political and strategic reasons.

Phosphorites have been considered a likely source for petroleum (McKelvey, 1959 and Brongersma-Sanders, 1948) but only recently has the nature of the organic matter contained in phosphatic sediments been studied (Powell et al., 1975). The association between the extensive South African phosphorite deposits and possible petroleum accumulations awaits further study.

CHAPTER V. SUMMARY OF MAIN CONCLUSIONS

The main conclusions drawn in the preceding three chapters are summarized below.

5.1. The unconsolidated sediments

The surficial sediments on the continental margin off the Cape west coast represent several ages and modes of deposition. The sedimentary character has been considerably influenced by erosion during Tertiary transgressive/regressive cycles and modern terrigenous processes are dominant only in the nearshore regions. Shelly quartzitic sands and gravelly sands partially fill hollows and depressions on the nearshore platform, and occasionally cobbles and boulders of (?) Malmesbury shale and Cape Granite litter its surface. The benthonic foraminifera Quinqueloculina sp. and Elphidium sp. commonly inhabit these sediments. The absence of a Nearshore Modern Sand Prism (Swift, 1969) on the coastal platform indicates that only very small quantities of coarse sediment are presently being deposited in the marine environment. Most of the sand is trapped in estuaries where some becomes available for littoral and aeolian transport.

Since the sea reached its present level 6 to 7 000 years ago (Curray, 1965), a lens of organic-rich mud ($\sim$5% C_{org}) up to 15 metres thick has accumulated at the base of the coastal platform. Large quantities of this sediment are being aggregated into faecal pellets by polychaete worms such that over 90% of the coarse fraction is commonly composed of these pellets. Diatoms, and the benthonic and agglutinated foraminifera, Ammonia beccarii, Discammina sp., Cyclammina sp. and Haplophragmoides sp. are characteristic of this sediment type.

The mud content gradually decreases seawards until on the inner shelf the sediment is dominated by well sorted, very fine quartzitic sand. This blanket of terrigenous detritus thins rapidly and eventually wedges out onto a Tertiary erosional surface on the mid shelf. The absence of modern detritus on the outer parts of the shelf is in accord with Emery's (1968) estimate that over 70% of the worldwide shelf sediments are relict.

There is much debate as to what happens to the suspended material once it reaches the marine environment. It is either restricted to the nearshore zone or it may bypass the outer shelf and be deposited on the slope or in the ocean basins. A sharp boundary between the terrigenous muddy sands on the inner shelf and the thin veneer of highly calcareous sediment mantling the rocky mid shelf north of Saldanha Bay, suggest that very little fine material derived from the continent is crossing the shelf, or if it is, then it is 'leap frogging' the outer margin (Schubel and Okubo, 1972). A constant decrease in the mud content seawards off the Olifants River suggests that fine

terrigenous material may presently be prograding across the inner shelf by diffusion, a process of continual deposition and resuspension.

The well-sorted quartz sand which mantles extensive regions of the inner shelf has probably resulted from a process of sediment fractionation. Data which have recently become available suggest that very fine sand on the shelf may be transported seawards in suspension under severe storm conditions, whereas coarser material moves more slowly as bedload which has a net onlandward transport direction. Such a selective mechanism may have been responsible in preferentially concentrating sediment of this grade during the Pleistocene.

Glauconite and phosphorite sands and gravels fill depressions on the rocky mid shelf off Saldanha Bay and the Cape Peninsula, but west of Hondeklip Bay these authigenic minerals are considerably diluted by biogenic carbonate deposition. Glauconite constitutes over 80% of the sediment over extensive areas off Saldanha Bay and the P_2O_5 values in this region are approximately 5 to 6%. Regionally glauconite and apatite are closely related except off Hondeklip Bay where the deposits are offset. Well-rounded and abraded black glauconite dominates the sediments of the mid shelf but the less robust yellow-green and blue-green glauconite as well as foraminiferal casts are more common in outer shelf and upper slope sediments. Black glauconite is probably eroded from Tertiary glauco-phosphorites during a late Tertiary regression/transgression and light green glauconite is closely related to Cretaceous or lower Tertiary outcrops.

Calcareous sands and muddy sands containing mainly foraminifera and coccolithophorids (Rogers, 1972) mantle the outer parts of the continental margin north of Saldanha Bay, but to the south the shelf is largely devoid of biogenic and terrigenous sediment. The benthonic and agglutinated foraminifera Florilus boueaum, Martinottiella sp. and Sigmoilopsis sp. are typical of the foraminiferal sands of the shelf sediments to the north, and the slope sediments are characterized by Orbulina universa, Pyrgo sp., Siphotextularia sp., Vulvulina sp., Reophax agglutinatus, and Gaudryina sp. or Migros sp.

Sediments on the western Cape shelf can therefore be seen to form distinct belts paralleling the coast, except off the Olifants River where a broad swathe of very fine quartz sand mantles the entire shelf width. This region effectively separates the predominantly calcareous sediments on a broad shelf in the north from a narrow shelf covered mainly in authigenic sediment in the south.

5.2. Mineralogy and geochemistry of the clay fraction

The clay mineral assemblage is characterized by abundant illite (50-90%); subordinate montmorillonite (10-30%) and kaolinite (5-20%); and minor chlorite (<5%). Although more marked regional variations occur onland, approximately the same proportion of clay minerals is found in the adjacent onland shales and in the sediments of the rivers draining the hinterland. A well-developed seaward distribution of clay minerals is observed. Illite is richest close to the coast, followed by kaolinite which is most abundant on the outer shelf, whereas the highest concentration of montmorillonite occurs in the slope sediments. This distribution is in keeping with the known settling and flocculation characteristics of these minerals.

Ni, Zn and possibly Pb are more abundant in the marine clays (<2μm) than in the <2μm fraction of the onland shales and river sediments. From partition studies it is apparent that the additional fraction of these elements is concentrated in the marine sediments by biogenous process in areas of upwelling. The concentration of these elements is not as high as that reported by Calvert and Price (1970) for regions of intense nearshore upwelling off South West Africa. This is due to the relatively lower biological activity occurring on the shelf off the Cape west coast.

Al, K, Fe, and Mn are generally more abundant in the source rocks and in the river sediments, and on the continental shelf their concentrations decrease markedly seawards. Al is less abundant in the marine environment possibly owing to Al^{++}/Fe^{++} substitution and K is depleted possibly because of degradation and/or K desorption of illitic clay. The majority of the Fe is associated with the detrital fraction, but Mn is transported mainly in the oxidate phase which is readily desorbed immediately it enters the marine environment. Ca in the marine clays is derived through the breakdown of calcareous organisms.

Although the considerable differences in the onland geology are to a certain extent reflected in the composition of the <2μm fraction in the river sediments, no marked latitudinal variations in the marine clay mineral and geochemical assemblage is apparent. Climatic changes in the hinterland also have had no obvious effect on the off-shore clay mineralogy or geochemistry. The absence of well-defined dispersal patterns could be due to the effect of the northward Benguela Current, the lack of major differences in the material entering the marine environment or it could be due to the relatively small quantity of sediment being supplied to the continental margin.

5.3. The nature and origin of the glauconite and phosphorite deposits

The rocks which cover extensive areas of the mid and the outer shelves off the Cape west coast are generally phosphatic (>5% P_2O_5). The distribut-

ion, mineralogy and geochemistry of these deposits were subjected to detailed investigations.

Phosphatized microfossiliferous limestones (NI type) containing negligible glauconite and quartz form the largest group of rocks recovered from the shelf. These phosphorites are found throughout the area, but no distribution trends are apparent. The cement of some NI phosphorites off the Cape Peninsula and west of Saldanha Bay are partly glauconitic. Glauconitic NIII and CI phosphorites are most common off the Cape Peninsula and off Saldanha Bay and those recovered from regions farther north are notably glauconite-poor. Only a small number of ferruginous phosphorites have been recovered and most of these were dredged from the "glauconite-poor" areas north of Saldanha Bay. Goethite replaces glauconite as being the most dominant iron-bearing mineral present in these rocks.

The composition of the phosphorite has had a significant influence on the nature of the overlying sediment. The most phosphatic unconsolidated sediment occurs in areas where phosphorite rock has been recovered. The potassium concentration of the surficial sediment drops markedly north of Saldanha Bay because the phosphorites, which are the source rock of the glauconite in the overlying sediment, contain only minor quantities of this mineral. Both the phosphate (P_2O_5) and glauconite (K_2O) are depleted in the sediments north of Saldanha Bay owing to carbonate dilution.

The phosphorites have an average P_2O_5 content of 17,8% and are chemically and mineralogically similar to the Agulhas Bank deposits. They are composed mainly of collophane, glauconite, calcite and quartz. The chemical composition of the five phosphorite types is dictated mainly by variations in the abundance of the non-phosphatic components. Francolite is the primary phosphate mineral present. High F/P_2O_5 and CO_2 values for both the Agulhas Bank and Cape west coast phosphorites indicate that additional fluorine has been introduced into the apatite structure to restore the charge balance caused by CO_3^{2-}/PO_4^{3-} substitution. Microprobe investigations have revealed the ubiquitous presence of silt-size quartz and finely disseminated (<1µm) glauconite in the matrix of phosphorite rocks. Lime-green cement of some phosphorites contains more than 3% K_2O.

Quartzitic phosphorites occur onland in the coastal lowlands between the Olifants River and Bokpunt, but are most abundant in the Saldanha Bay region. Onland phosphorites contain minor phosphatized shell/bone and heavy minerals set in a light brown collophane cement. These rocks have been eroded to form extensive deposits of pelletal phosphorite. A small isolated deposit of phosphatized coquina is also present at Hoedjiespunt near Saldanha village. Microprobe and bulk chemical analyses indicate that the composition of the basal Miocene quartzitic phosphorite of the Saldanha Formation is

dissimilar to surrounding more elevated phoscrete deposits. Phoscretes have probably been formed in the same manner as calcretes, by the upward percolation of phosphate-rich water which evaporates at the surface depositing apatite in the interstices of the sediment. The onland phosphorites contain abundant quartz whereas the off-shore deposits are characterized by plentiful glauconite and calcite.

The onshore deposits have been formed by interstitial precipitation of carbonate apatite in a manner considered analogous to present-day phosphorite diagenesis in the diatomaceous muds off South West Africa. Wind-accelerated upwelling provided nutrients to support periodic blooms of mainly siliceous phytoplankton in the nearshore region. Collapse of upwelling cells during calms resulted in mass mortalities and the accumulation of vast amounts of phosphorous-rich organic matter on the sea floor. Phosphate is precipitated interstitially under conditions similar to those envisaged by Burnett for the Chilean-Peruvian deposits and by Senin and Baturin for the South West African occurrences.

Minor pelletal phosphorite occurrences near the shelf break in the vicinity of Childs Bank and south of Cape Point are probably intermittent extensions of the rich outer shelf pelletal deposits to the north. The pelletal phosphorites have probably been formed under similar conditions as those envisaged for the South West African deposits, that is by precipitation in an anaerobic environment.

Deposition of mainly zooplankton from the less nutritious waters of the open shelf has resulted in the accumulation of large quantities of predominantly calcareous organisms on the sea floor on the mid and the outer parts of the continental margin. Although the input of phosphorous is insufficient to cause precipitation, lime mud is readily replaced to form a cryptocrystalline carbonate apatite cement (francolite). Under these conditions all the components of the bottom sediment, including glauconite, foraminifera, minor quartz, clay minerals and skeletal debris are lithified to form a phosphorite rock, sometimes referred to as a "phosphatic pavement". The matrix thus comprises a heterogeneous mixture of minerals, the composition of which varies according to the sedimentological environment, whereas pelletal phosphorite cement contains a lower non-phosphatic component because it originates by interstitial precipitation. Glauconitic NIII phosphorites formed when the deposition zones migrated landwards in response to a rising sea level thereby allowing calcareous sediment to be deposited in regions rich in glauconite. Some phosphorites have retained a degree of layering, but more frequently bioturbation has produced a random mixture of components. Inclusion of NI phosphorite fragments in the bottom sediment has resulted in a conglomeratic phosphorite texture.

Micro-analysis of unaltered and uncontaminated glauconite has revealed that it is rich in K and Mg in relation to glauconite from other localities. It is also relatively depleted in Na possibly because of the non-apatitic nature of the analysed material. In the process of glauconitization Fe substitutes for Al and the change in lattice charge is accounted for by adsorption of interlayer K. Although a general decrease in the Al content accompanies K enrichment, the data indicate that the Fe is emplaced in clay structure early in the glauconitization process, probably by a mechanism which is independent of and prior to the fixation of K. A systematic relationship between K_2O and MgO supports a recent contention that some Mg is located in the interlayer position.

The majority of "glauconite" is composed of a mixture of apatitic and glauconitic material, and non-phosphatic pellets are dominant only in the nearshore deposit off Hondeklip Bay. The mode of glauconite formation remains obscure and any diagenetic model would have to take into account the mixed mineral grains, the source of the Fe required by the glauconite structure, and the formation of the pellet itself. The size and the morphology of the majority of glauconite grains exclude the possibility of their forming by alteration of faecal pellets or as foraminiferal infillings, or by the replacement of any non-clay mineral. Alteration of a degraded clay is considered to be the chief diagenetic mechanism for glauconite mineralization.

A theory involving aggregation of colloidal proto-glauconite and apatite is attractive and could be invoked to explain the origin of these deposits. However, there is evidence to indicate that at least some of the glauconite and mixed mineral pellets have originated directly by alteration of the bottom sediment either before or after disaggregation. Heterogeneous mixed mineral grains from the Childs Bank region have clearly originated by fragmentation of the surrounding phosphorite bedrock. The margins of mottled or variegated pellets have frequently been strongly glauconitized subsequent to the formation of the grain, and the reorganisation of the apatite phase has resulted in dilation cracks being filled with collophane and in the grain surface being coated in a pure apatite pellicle. The unaltered core of these grains is similar in composition to that of a glauco-phosphatic matrix. In some localities immature non-phosphatic glauconites commonly contain silt-size quartz, foraminiferal tests and even unaltered calcite. Incorporation of non-colloidal material with the proto-pellet would be contrary to the theory of colloidal aggregation. Although it seems that at least some glauconites and mixed-mineral material were formed by alteration of the bottom sediment before or after disaggregation, the relative importance of this mechanism remains an open question.

The medium to coarse sand-size glauconite grains in the nearshore region off Hondeklip Bay could have been formed only by colloidal aggregation or by disaggregation of semi-consolidated clay-rich bottom sediments. It is significant that these non-phosphatic glauconites occur in sediment devoid of calcitic debris.

The most immature glauconite contains approximately 20% Fe_2O_3, but the Fe_2O_3 content of the <2μm fraction of Modern glauconitic sediment is less than 8% (on a carbonate-free basis). It is clear that additional Fe is required before glauconitization will occur. The distribution of Fe in shelf clays is related to terrestrial input, but even the <2μm sediment presently being introduced into the marine environment contains less than 10% Fe_2O_3. Moreover, the distribution of glauconite off the coasts of southwest Africa suggests that its formation is related to regions of upwelling and low sedimentation, and not to areas of terrestrial input. The mechanism of Fe enrichment is unknown, but the frequent occurrence of mixed mineral grains and of pelletal phosphorite showing glauconitized margins indicates that under favourable conditions Fe may be extracted directly from the interstitial waters. Clay is at present not being enriched in Fe by fluvial or biogenous processes, but a common association of glauconite formation with unconformities suggests that these conditions may occur during transgressive/regressive periods.

Two main periods of phosphatization have been proposed for the Tertiary, namely the U. Eocene and the M. Miocene, whereas glauconite formation occurred in M. Miocene/L. Pliocene times. Neither the glauconite nor the phosphate deposits are regarded as economically viable at the present time.

A P P E N D I X I

SAMPLES RECOVERED FROM THE CAPE WEST SHELF.

ABBREVIATIONS

G - grab sample

G.C. - small gravity core sample

P.C. - piston core sample

T.C. - trigger core sample

(1) - no sample, rocky bottom

(2) - very small sample, rocky bottom

(3) - too small for analysis

(4) - too small for analysis, rock recovered.

(5) - rocky bottom, rock recovered.

MARINE SAMPLES

STATION NO.	SAMPLE TYPE	LATITUDE (SOUTH) degs.	mins.	LONGITUDE (EAST) degs.	mins.	DEPTH (m)	DISTANCE FROM SHORE (n.miles)
CRUISE 118							
100	G	33	54,4	18	06,5	154	11,5
101	G	33	57,7	18	02,2	174	13,5
102	G	33	59,9	17	57,0	208	17,0
103	G	34	02,3	17	52,6	249	20,5
104	G	34	04,0	17	43,3	284	30,0
105	G	34	07,3	17	42,1	343	30,5
106	G	34	10,0	17	37,2	451	36,0
108	G	34	18,6	17	33,1	905	40,0
109	G	34	18,5	17	39,6	476	34,0
110	G	34	16,9	17	47,8	331	27,5
111	G	34	13,5	17	54,7	280	20,0
112	G	34	10,5	18	00,9	238	15,0
113	G	34	08,4	18	06,0	200	10,5
CRUISE 121							
129	G	33	49,6	18	09,4	130	11,0
130	G	33	53,5	17	58,9	177	17,0
131	G	33	46,3	17	47,8	216	30,0
135	G	33	46,7	17	58,6	172	21,0
136	G	33	40,8	17	44	249	30,0
CRUISE 123							
145	G	33	43,6	18	19,9	55	5,0
146(1)	G	33	33,7	18	04,5	-	10,0
147	G	33	24,4	17	42,3	187	21,0
149	P.C.	33	30,0	16	42,9	1325	67,0
CRUISE 127							
168	G	33	56,8	18	19,8	50	2,0
169	G	34	05,6	17	58,1	222	17,0
170	G	34	05,7	18	12	138	6,0
171	G	34	03,8	18	16,6	91	2,0
172	T.C.	34	36	17	32	2147	46,0
173	T.C.	34	34,7	17	38,9	1464	40,5
174	G	34	33,8	17	49,3	650	32,0
175	G	34	26,9	18	00,2	320	21,0
176	G	34	23,7	18	10,6	290	12,0
177	G	34	30	18	20	310	12,0
178	T.C.	34	37,6	17	59,4	600	27,0
179	T.C.	34	15,3	16	53,4	3399	72,5
CRUISE 131							
200	G	33	40	18	10,6	83	10,0
201	G	33	35	17	54,6	163	20,5
202	P.C.	33	27	17	22	780	40,5
204	T.C.	33	17	16	12	2520	86,0
205	T.C.	32	48	16	37	880	63,0
206	G	32	59	16	59	418	44,0
207	G	32	53	17	07	334	38,0
208	G	33	03,2	17	40,5	198	10,5
209	G	33	05,4	17	46	148	8,0
210	P.C.	33	20,2	17	24,0	578	33,0
CRUISE 142							
264	G	34	15,2	18	13,2	134	6,5
265	G	34	19,7	18	19,7	71	3,5
266	G	34	25,4	18	25,6	112	5,0
269	G	34	35	18	51,5	137	11,0
270	G	34	31	18	41	131	10,0
271	G	34	27	18	34,4	55	8,0
CRUISE 146							
286	G	34	12,5	18	05,4	225	12,0
287	G	34	19,0	17	56	308	21,0
288	P.C.	34	43	17	45	2292	39,0
290	G	34	29	18	03	302	20,5
292	G	34	42	18	12	204	24,0
295	G	34	53,7	18	21,5	380	33,0
296	G	34	48,7	18	31,2	207	29,5
297	G	34	42,5	18	41,3	170	27,5

STATION NO.	SAMPLE TYPE	LATITUDE (SOUTH)		LONGITUDE (EAST)		DEPTH (m)	DISTANCE FROM SHORE (n.miles)
		degs.	mins.	degs.	mins		
CRUISE 146 contued:							
298	G	34	39	18	50	150	15,5
299	G	34	47	18	39	182	25,0
300	G	34	56	18	36	227	34,5
308	G	34	54,2	18	08,8	1108	36,0
309	P.C.	34	41,2	17	53	1007	34,0
	T.C.	34	41,2	17	53	1007	34,0
311	G	34	31,5	18	26	184	10,0
312	G	34	36	18	18	400	16,5
CRUISE 148							
330	G	34	56,3	18	55	181	29,0
331	G	34	46	18	54,4	162	23,5
332	G	34	44,5	18	59,7	151	19,0
333(1)	G	34	39,8	18	59,6	-	25,0
334(1)	G	34	33,0	19	01	104	11,5
335	G	34	24	19	00,5	61	4,0
CRUISE 187							
833	G	34	05,3	18	16,6	91	2,0
CRUISE 219							
1675	G	34	59,5	18	57,0	190	29,5
1686	G	34	49	19	02,3	158	19,5
1687	G	34	51	18	51	180	27,5
1688	G	34	52	18	43	193	29,0
1689	G	34	42	18	36	179	21,0
1690	G	34	35	18	35,2	172	20,0
1691	G	34	34	18	29	220	13,5
1692	G	34	36	18	22	305	15,5
1693	G	34	45	18	22	359	25,0
1694	G	34	45	18	19,6	425	25,5
1695	G	34	45	18	17,5	440	26,0
1696	G	34	44	18	16	491	24,5
1697	G	34	46	18	15	545	27,5
1698	G	34	47	18	13	502	29,0
1699	G	34	41,5	18	04,8	395	28,0
1700	G	34	38,3	18	06,3	344	24,5
1701(2)	G	34	32	18	10	318	17,0
1702	G	34	21	18	12,5	305	9,5
1703(1)	G	34	19	18	17,5	-	5,0
1704(1)	G	34	17,2	18	18,5	-	3,5
1705	G	34	20	18	07	262	13,0
1706(1)	G	34	20,7	17	58,8	-	20,5
1710	G	34	14	18	09,8	235	13,0
1711	G	34	14,8	18	08,5	232	9,0
1712(1)	G	34	8,5	18	14,9	-	1,5
1713	G	34	08,7	18	10,3	173	7,0
1714	G	34	07,5	17	56,5	250	18,5
1715	G	34	06,5	17	38	351	33,0
1716(1)	G	34	07	17	28	-	41,0
1717	G	33	46,5	17	39	251	35,0
1718	G	33	45,8	17	47	219	29,5
1719	G	33	45,7	17	50,5	198	26,0
1720	G	33	46,3	17	58	165	21,5
1721	G	33	47,4	18	08,8	125	15,0
CRUISE 236							
2203	G	33	52	18	06	140	12,0
2204(1)	G	33	51,6	18	04,6	-	15,0
2205	G	33	52	17	47	270	27,5
2206	G	33	36	17	44	200	27,0
2207	G	33	26	17	59	130	17,0
2208(1)	G	33	36	18	12	-	5,5
2209	G	33	25	18	06	20	6,0
2210(1)	G	33	32	18	15	-	2,0
2211	G	33	36,4	18	17,3	40	4,5
2221	G	33	07	17	37	225	15,5
2222	G	33	08,1	17	46,6	155	8,5
2223(1)	G	33	07	17	51	95	5,0
2224	G	33	09,4	17	57,3	58	2,5
2226(1)	G	33	14	17	53	-	7,0
2227	G	33	14	17	50	145	10,0
2228	G	33	13,4	17	43,4	174	14,0

STATION NO.	SAMPLE TYPE	LATITUDE (SOUTH)		LONGITUDE (EAST)		DEPTH (m)	DISTANCE FROM SHORE (n.miles)
		degs.	mins.	degs.	mins.		
CRUISE 236 contd.							
2229	G	33	12,9	17	36	305	20,5
2230(1)	G	33	12,7	17	30	370	22,0
2231(1)	G	33	11	17	23	450	27,0
2232(1)	G	33	11	17	10	452	33,0
2233	G	33	10,5	16	56	655	49,0
2235(1)	G	33	28	17	28	640	32,5
2236(2)	G	33	00	17	50	58	2,0
2237	G	33	00,0	17	46,2	145	5,0
2238	G	33	00,0	17	40	185	10,5
2239	G	33	00,0	17	33	320	16,0
2240	G	33	01	17	25	325	23,0
2241	G	33	02	17	14	355	32,0
2242	G	33	04	17	03	460	41,0
2243	G	32	55	16	51	500	50,5
2244	G	32	57,8	16	57,5	418	46,0
2245	G	32	51	17	03	340	41,5
2246	G	32	49	17	13	315	33,0
2247	G	32	50	17	22	300	26,5
2248	G	32	49	17	25	280	23,0
2249	G	32	48	17	30	260	19,0
2250(1)	G	32	54	17	46,3	80	3,5
2251	G	32	53	17	45	185	6,0
2252	G	32	54	17	38	185	11,0
2253	G	32	53	17	34	290	14,0
2254	G	32	53,2	17	28	270	20,0
2255(1)	G	32	49,5	17	48	70	3,0
2256(1)	G	32	45	17	50,4	60	3,5
2257	G	32	44,8	17	45,7	100	7,0
2258	G	32	45	17	39	202	13,0
2259	G	32	44	17	26	255	23,0
2260	G	32	45,5	17	13,2	303	34,0
2261(1)	G	32	46,5	17	00,5	325	44,5
2262	G	32	47,5	16	49	450	54,0
2264	G	32	33	16	32	520	70,0
2265	G	32	33	16	42	380	61,0
2266	G	32	32,5	16	49,5	330	56,0
2267	G	32	32	16	59,5	295	48,0
2268	G	32	32	17	07	280	42,0
2269	G	32	31,5	17	15	252	35,0
2270	G	32	31	17	27	210	26,5
2271	G	32	32,5	17	41,5	200	16,0
2272	G	32	32,5	17	51	65	10,5
2273	G	32	32,5	18	00	65	7,0
2274	G	32	32,5	18	12	37	5,0
2275	G	32	34,2	18	17,4	17	1,0
2276	G	32	23,7	18	18,2	32	1,0
2277	G	32	24	18	06,3	81	11,5
2278	G	32	24	17	54	105	18,5
2279	G	32	24	17	42	178	22,0
2280	G	32	27	17	31,5	192	27,0
2281	G	32	28,2	17	20	253	33,5
2282	G	32	29,5	17	06	295	43,0
2283	G	32	31,2	16	54,5	330	52,0
2284	G	32	32,5	16	42	370	61,5
2286	G	32	21,5	16	31	410	73,0
2287	G	32	21	16	40	345	67,0
2288	G	32	20	16	51	300	60,0
2289	G	32	18	17	02	260	51,5
2290	G	32	17	17	14	210	45,0
2291	G	32	15	17	28	180	37,0
2292	G	32	13	17	35	165	35,0
2293	G	32	13	17	35	145	30,5
2294	G	32	13	17	59	119	18,0
2295	G	32	14	18	11	88	7,0
CRUISE 239							
2326	D	32	19,6	18	17,5	22	3,5
2327(1)	G	32	07	18	15,5	50	4,0
2328	G	32	04,5	18	12,7	92	5,0

STATION NO.	SAMPLE TYPE	LATITUDE (SOUTH) degs.	mins.	LONGITUDE (EAST) degs.	mins.	DEPTH (m)	DISTANCE FROM SHORE (n.miles)
CRUISE 239 contd.							
2329	G	32	04,5	18	01,2	120	14,5
2330	G	32	04	17	49,3	130	24,5
2331	G	32	03,4	17	37,5	153	33,0
2332	G	32	03,8	17	27	160	41,5
2333	G	32	04,5	17	15	185	51,0
2335	G	31	58	17	02,5	238	56,0
2336	G	31	57,5	17	14,2	180	49,0
2337	G	31	57	17	26	153	40,0
2338	G	31	56,5	17	37,4	143	33,0
2339	G	31	56	17	44	130	27,0
2340	G	31	55,5	18	01	116	12,0
2341	G	31	56	18	12,6	84	3,5
2342	G	31	50	18	12	75	3,0
2343	G	31	50	18	00,4	111	13,0
2344	G	31	50	17	48,5	128	21,0
2345	GC	31	50	17	37,1	156	28,5
2346	GC	31	47	17	26	143	33,5
2348	GC	31	43,5	17	02	246	49,0
2349	G	31	34	16	59	277	47,0
2350	GC	31	32,2	17	11	228	38,0
2352	GC	31	29,6	17	33,8	128	20,0
2353	G	31	28,8	17	57	99	5,0
2354	G	31	34,5	18	01,2	98	3,0
2355	G	31	40	18	05,5	87	3,5
2356	G	31	40	17	57,6	115	9,5
2357	G	31	40	17	46	126	17,0
2358	G	31	39,8	17	34,2	133	24,5
2359	G	31	39,5	17	23,8	144	31,5
2360	G	31	39,3	17	11,2	210	40,5
2361	G	31	18,8	16	57,5	241	44,5
2362	G	31	18,6	17	03,2	219	36,5
2363	G	31	18,4	17	15	192	28,0
2364	G	31	18,2	17	27	177	19,0
2365	G	31	18,2	17	36,8	134	12,0
2366	G	31	18,2	17	48,2	101	5,0
2367	G	31	10	17	38,5	130	7,0
2368	D	31	10	17	27,8	155	15,0
2369	G	31	09,2	17	13,8	188	23,5
2370	G	31	08,4	16	59,5	200	34,0
2371	G	31	07,8	16	45,5	238	44,0
2372	G	31	07	16	32	258	52,5
2373	G	30	55	16	24	260	54,5
2374	G	30	53	16	36	243	45,0
2375	G	30	51,5	16	45,5	216	36,5
2376	G	30	50	16	57,8	180	27,5
2377	G	30	50	17	09,5	165	18,5
2378	G	30	50	17	21	142	10,5
2379(1)	G	30	50	17	31	30	3,5
2380(1)	G	30	54,4	17	33,8	40	1,0
2381	G	31	00	17	35	115	6,0
2382	G	31	00	17	24	165	12,0
2383	GC	31	00	17	12,5	185	21,0
CRUISE 244							
2432	G	33	53,5	17	58	180	17,5
2433	GC	33	53,5	17	52	270	22,0
2434	GC	33	52,5	17	46	248	27,5
2435	GC	33	52	17	38,5	274	33,0
2436	GC	33	51	17	31	310	40,5
2437	GC	33	51	17	27,5	440	43,0
2438	G	33	50,5	17	24,2	680	45,0
2439(3)	G	33	50	17	21	1025	49,0
2440	G	33	14,5	17	09	450	39,0
2441	G	32	40	17	35	232	16,0
2442	G	32	40	17	20	270	28,0
2443	G	32	39	17	05,3	300	40,0
2444	G	32	39	16	47,5	381	55,0
2445	G	31	56	16	51	272	62,5
2446	G	31	56	16	39,5	310	71,5

STATION NO.	SAMPLE TYPE	LATITUDE (SOUTH) degs.	mins.	LONGITUDE (EAST) degs.	mins.	DEPTH (m)	DISTANCE FROM SHORE (n.miles)
CRUISE 244 contd.							
2447	G	31	55,5	16	28	350	79,5
2448	G	31	55,5	16	15,3	392	90,0
2449(1)	G	31	41,5	16	17,3	388	83,0
2450	G	31	41	16	21	325	80,0
2451	G	31	40,5	16	32,2	305	73,5
2452	G	31	44	16	52	282	58,0
2453	G	31	44	17	04,5	223	48,0
2454	G	31	34	17	04,5	245	43,0
2455	G	31	32,5	16	54	265	50,0
2456	G	31	31,5	16	44,5	285	56,0
2457	G	31	30	16	33,5	300	63,0
2458(3)	G	31	29	16	20	392	75,0
2459	G	31	14	16	23	300	64,0
2460	G	31	14	16	37,5	272	54,0
2461	G	31	19	16	41	270	52,0
2462(4)	G	31	19	16	21	310	67,5
2463	G	31	08,5	16	22,8	292	60,5
2464	G	31	06	16	11,5	284	68,5
2465	G	31	04	16	02,3	315	73,0
2466	G	31	01,5	15	22,8	285	102,0
2467	G	30	59,5	15	42,5	328	88,0
2470	G	30	45,3	15	33	348	90,0
2471	G	30	46	15	44	193	81,5
2472	G	30	46,5	15	55,5	203	72,5
2473	G	30	47	16	06,5	222	64,0
2474	G	30	47,5	16	18	268	55,5
2475	G	30	48	16	30	255	47,0
2476	G	30	49	16	42,5	240	38,5
2477	G	30	45	16	53	205	28,0
2478	G	30	45	17	05	182	17,0
2479	G	30	46,5	17	18	138	10,0
2480	G	30	45,8	17	24	129	5,5
2481	G	30	45	17	19	80	7,5
2482	G	30	58	16	57,5	192	31,5
2483	G	30	55	16	24,5	270	53,0
2484	G	30	55	16	12	290	63,0
2485	G	30	55	16	00	224	73,0
2486	G	30	55	15	48	195	81,0
2487(1)	G	30	55	15	36,7	200	94,0
2488	G	30	50,5	15	28	445	95,0
2489	G	30	36	15	28,5	310	91,0
2490	G	30	35	15	39	289	82,5
2491	G	30	35	15	51,5	255	73,0
2492	G	30	35	16	04	255	63,5
2493	G	30	35	16	15	252	54,0
2494	G	30	35	16	27	245	44,0
2495	G	30	35	16	38	222	36,0
2496	G	33	18,5	17	37,5	280	20,0
CRUISE 257							
2676	GC	32	07	15	23	2685	133,5
2677	GC	31	25	15	15	1662	119,5
2678	G	30	36	16	50	180	26,0
2679	G	30	35	17	01	160	18,0
2680	G	30	35	17	12	140	10,5
2681(1)	G	30	35	17	23	47	3,5
2682	G	30	27,3	17	18,6	36	2,5
2683	G	30	27	17	07	148	9,5
2684	G	30	33	16	56	170	20,0
2685	G	30	34	16	44	200	30,5
2686	G	30	35	16	33	212	39,0
2687	G	30	34	16	33	226	47,0
2688	G	30	30	16	11	240	54,5
2689	G	30	31	16	01	255	63,5
2690	G	30	31	15	50	271	72,0
2691	G	30	32	15	37	270	82,0
2692	G	30	31	15	26	293	91,5
2693	G	30	31	15	13	305	100,5
2694	G	30	30	15	01	447	113,0

STATION NO.	SAMPLE TYPE	LATITUDE (SOUTH) degs.	mins.	LONGITUDE (EAST) degs.	mins.	DEPTH (m)	DISTANCE FROM SHORE (n.miles)
CRUISE 257 contd.							
2695	GC	30	30	14	47	590	126,5
2696	GC	30	29	14	35	840	136,5
2697	GC	30	17	14	19	940	141,5
2698	GC	30	15	14	30	650	144,5
2699	GC	30	14	14	41	500	126,0
2700	GC	30	13	14	51	469	119,0
2701	G	30	11	15	04	395	105,5
2702	G	30	09	15	16	253	95,0
2703	G	30	08	15	26	220	87,0
2704	G	30	06	15	36	218	79,0
2705	G	30	05	15	46	200	70,0
2706	G	30	05	15	57	185	62,0
2707	G	30	05	16	09	175	51,5
2708	G	30	05	16	20	178	42,0
2709	G	30	04	16	30	180	34,0
2710	G	30	04	16	41	150	24,5
2711	G	30	04	16	52	130	16,0
2712	G	30	04	17	07	95	3,5
2713	G	30	18	17	15	111	2,5
2714	G	30	20	17	01	150	11,5
2715	G	30	21	16	49	173	22,0
2716	G	30	23	16	38	198	31,5
2717	G	30	24	16	26	220	43,0
2718	G	30	25	16	15	230	52,0
2719	G	30	27	16	04	240	60,0
2720	G	30	26	15	53	250	70,5
2721	GC	30	24	15	41	256	80,0
2722	GC	30	22	15	30	265	87,5
2723	GC	30	18	15	04	420	109,0
2724	GC	30	14	14	53	475	120,0
2725	GC	30	12	14	42	538	128,0
2726	GC	30	05	14	50	485	122,0
2727	GC	30	06	14	36	530	131,0
2728	GC	30	06	14	24	830	143,0
2758	G	33	17	17	56	100	10,5
2759	G	33	37	18	08	105	11,0
2760	G	33	44	18	03,5	130	17,5
CRUISE 259							
2762	GC	33	12	17	42	175	15,0
2763	GC	33	11,4	17	39,2	225	15,5
2764	GC	33	11,4	17	37,2	260	17,5
2765	GC	33	10	17	35,4	320	18,5
2766	GC	33	10	17	33	358	20,0
2767	GC	33	10	17	31	359	21,0
2768	GC	33	10	17	29,5	453	22,5
2769	GC	33	09,5	17	28	510	23,0
2770	GC	33	09,5	17	27,5	436	23,5
2771	GC	33	09,5	17	27,5	410	25,0
2772	GC	33	09	17	24	380	26,0
2773	GC	33	09	17	20	375	29,0
2774	GC	33	09	17	15	446	32,5
2775	GC	33	08,5	17	09,5	455	37,5
2776	GC	33	08,5	17	07	460	39,5
2777	GC	33	08	17	03,5	450	41,5
2778	GC	33	15	17	06	538	42,0
2779	GC	33	14,5	17	10,5	480	38,0
2780	GC	33	14,5	17	15	476	34,5
2781	GC	33	14	17	19	438	32,0
2782	GC	33	14	17	22	410	30,0
2783	GC	33	13,5	17	25	445	27,5
2784	GC	33	13,5	17	26	446	26,5
2785	GC	33	13,5	17	27	570	25,5
2786	GC	33	13,5	17	29	385	24,5
2787	GC	33	13,5	17	33	390	22,0
2788	GC	33	19	17	40	225	20,0
2789	GC	33	19	17	44	184	18,0
2790	GC	33	27,5	17	47,5	178	19,0
2791	GC	33	27	17	45	190	21,5

STATION NO.	SAMPLE TYPE	LATITUDE (SOUTH) degs.	mins.	LONGITUDE (EAST) degs.	mins.	DEPTH (m)	DISTANCE FROM SHORE (n.miles)
CRUISE 259 contd.							
2792	GC	33	27	17	40	200	25,0
2793	GC	33	27	17	37	220	27,0
2794	GC	33	27	17	31	380	31,0
2795	GC	33	27	17	28,5	430	32,5
2796	GC	33	27	17	27,5	442	33,5
2797	GC	33	27,5	17	27	451	33,5
2798	GC	33	27,5	17	26	465	34,5
2799	GC	33	27,5	17	25	610	35,0
2800	GC	33	27,5	17	23,5	760	36,0
2801	GC	33	27,5	17	22,5	685	37,0
2802	GC	33	27,5	17	19	750	39,0
2803	GC	33	27,5	17	17	520	41,0
2804	GC	33	27,5	17	13	560	43,0
2805	GC	33	28	17	03	800	50,5
2806	GC	33	35,5	17	20,5	847	43,0
2807	GC	33	35,5	17	26	480	39,5
2808	GC	33	35,5	17	31	338	37,5
2809	GC	33	35,5	17	37	240	31,0
2810	GC	33	35,5	17	44	212	26,0
2811	GC	33	35,3	17	50,2	190	22,0
2812	GC	33	44	17	52	186	26,5
2813	GC	33	45,5	17	44,5	220	32,0
2814	GC	33	45	17	38	250	36,5
2815	GC	33	46	17	30	342	42,5
2816	GC	33	46	17	26	520	45,0
2817(3)	GC	33	46	17	19	1065	50,0
2818	GC	33	46	17	16	1026	51,5
2819	GC	33	46,5	17	13,5	1108	53,5
2820	GC	33	51	17	16	1148	53,0
2821	GC	33	56	17	19	1460	50,0
2822	GC	33	56,5	17	23,5	990	46,5
2823	GC	33	57	17	28,8	730	42,0
2824	GC	33	57	17	30,2	480	40,0
2825	GC	34	06	17	36	380	36,0
2826	GC	34	06	17	30	800	41,5
2827	GC	34	06	17	25	1415	44,5
2828	GC	34	06	17	23	1530	46,5
2829	GC	34	06	17	21	1520	48,0
2830	GC	30	06,5	17	16	2050	52,0
2831	GC	34	17	17	22	1800	48,5
2832	GC	34	16,5	17	24,5	1480	46,0
2833	GC	34	16,5	17	27	1210	44,5
2834	GC	34	16	17	30	920	42,0
2835	GC	34	16	17	34	660	38,0
2836	GC	34	25	17	43	582	34,0
2837	GC	34	27	17	39	1105	38,0
2838	GC	34	30	17	33	1520	43,0
CRUISE 261							
2840	G	30	55	15	42	204	89,0
	GC	30	55	15	42	205	89,0
2843	G	30	57	15	44	208	88,5
CRUISE 268							
3075	G	33	30,5	18	11	58	5,5
3076(5)	G	33	16	18	01	71	5,0
3077	G	33	11	17	56,5	85	4,0
3078(1)	G	33	04,3	17	51,3	-	2,5
3079	G	32	50,2	17	43,8	138	7,5
3080(1)	G	32	37,7	17	50,6	58	6,0
3081(1)	G	32	37,7	17	50,6	150	16,0
3082	G	32	28,3	17	57	90	13,5
3083(1)	G	32	30	17	58	85	11,5
3084(1)	G	32	32	17	59,2	72	11,0
3085	G	32	33,6	18	00,3	64	9,0
3086	G	32	35,5	18	01,5	54	7,5
3087	G	32	37,2	18	02,5	42	6,0
3088(1)	G	32	39	18	03,7	29	5,0
3089	G	32	41	18	05	18	4,5
3090	G	32	42,8	18	06	14	4,0

STATION NO.	SAMPLE TYPE	LATITUDE (SOUTH) degs.	mins.	LONGITUDE (EAST) degs.	mins.	DEPTH (m)	DISTANCE FROM SHORE (n.miles)
CRUISE 268 contd.							
3091	G	32	44	18	07	9	3,0
3092(1)	G	32	37	18	08,5	24	6,5
3093	G	32	29	18	10	54	7,5
3094	G	32	15	18	16	50	4,0
3095	G	32	04,7	18	17,0	9	1,0
3096(1)	G	32	04,6	18	17,2	33	3,0
3097	G	32	04,5	18	16,2	50	5,0
3098	G	32	04,3	18	15,8	60	7,5
3099	G	32	05,2	18	10,5	98	10,5
3100	G	32	03	17	39	150	32,0
3101	G	32	00	17	12,5	196	52,0
3102	G	32	00	17	01	251	60,5
3103	G	32	01	16	49	294	68,5
3104	G	32	01,5	16	38	344	77,0
3105	G	32	02	16	26	388	85,5
3107	GC	32	03	16	03	875	103,5
3108	GC	32	04	15	52	1245	112,0
3109	GC	31	54	15	54	900	108,0
3110	GC	31	43	15	57	628	102,0
3111	GC	31	32	16	01	510	91,0
3112	GC	31	27	15	46	648	98,5
3113	GC	31	22	15	35	840	102,5
3114	GC	31	16	15	21	1228	112,5
3115	GC	31	11	15	11	1640	119,5
3117	GC	30	47	15	06	1680	114,0
3118	GC	30	38	15	02	900	116,0
3297	G	30	35,5	17	23	88	4,5
3298	G	30	35,2	17	20,5	117	5,0
3299	G	30	35,2	17	18,5	124	6,0
3300	G	30	38,2	17	16,3	130	9,0
3301	G	30	35,2	17	13,8	134	9,5
3302	G	30	50,3	17	27,3	124	5,0
3303(1)	G	31	05,6	17	40,8	293	2,5
3304	G	31	05,3	17	38,8	88	4,5
3305	G	31	05,3	17	36,2	116	6,0
3306	G	31	05,3	17	34	128	8,0
3307	G	31	05,3	17	31,7	132	10,0
3308	G	31	05,5	17	28,8	132	12,5
3309	G	31	14,7	17	38,8	125	9,5
3310	G	31	14,7	17	41,2	120	8,0
3311	G	31	14,7	17	43,5	110	6,0
3312	G	31	15	17	45,6	80	3,0
3313(1)	G	31	15,0	17	48,9	38	1,5
3314	G	31	30,8	17	51,3	112	7,5
3315	G	31	30,8	17	53,7	109	5,5
3316	G	31	30,8	17	56	102	4,5
3317	G	31	30,8	17	58,5	90	3,5
3318	G	31	30,8	18	00,5	62	0,5
3319	G	31	45,4	18	11,2	35	2,0
3320	G	31	45,4	18	09	72	4,0
3321	G	31	45,5	18	06,6	90	5,5
3322	G	31	45,5	18	04,3	100	7,5
3323	G	31	45,5	18	02	104	9,5
3324	G	32	16,5	18	18,5	30	2,5
3325(1)	G	32	16,5	18	13,7	55	6,0
3326(1)	G	32	16,7	18	11,2	65	8,0
3327	G	32	16,3	18	07,8	95	11,0
CRUISE 273							
3337	GC	33	37	17	03	1209	54,5
3338	GC	33	22	16	53,5	990	55,5
3339	GC	33	13,0	16	33,0	1472	68,0
3340	GC	32	54,8	16	32,8	1335	65,5
3341	GC	32	41	16	31	945	69,0
3342	GC	32	30,5	16	11	1445	86,5
3343	GC	32	13,8	15	57	1368	102,0
3344	GC	31	48	15	37	1430	111,0
3345	GC	31	35,5	15	37	847	106,5
3346	GC	31	07,2	15	34,5	728	100,0
3347	GC	31	03	15	02	2030	122,0
3348	GC	30	42	14	49	1575	128,0

STATION NO.	SAMPLE TYPE	LATITUDE (SOUTH)		LONGITUDE (EAST)		DEPTH (m)	DISTANCE FROM SHORE (n.miles)
		degs.	mins.	degs.	mins.		
CRUISE 273 contd.							
3349	GC	30	29,5	14	25,5	1640	144,5
3350	GC	30	09	14	07	1650	158,5
3573	GC	30	13	15	39,4	234	79,0
3574	GC	30	13	16	02	211	61,5
3575	GC	30	14	16	24	198	41,5
3576	GC	31	08	15	52	437	85,5
3577	GC	31	22	16	05	453	82,0
3578	GC	31	42	16	09	420	90,0
3579	GC	31	59	16	17,5	420	90,5
3580	GC	32	10	16	23,5	386	85,0
3581	GC	32	08	16	41	320	72,0
3582	GC	32	06	17	00	242	61,0
3583(1)	G	33	05,8	17	48,9	92	5,5
3584	G	33	09,6	17	44,4	92	10,5
3585	G	33	11,5	17	42,2	169	13,0
3586	G	33	27	17	53,7	174	14,0
3587	G	33	59,7	18	08,9	157	7,5
3588(1)	G	34	00	18	11	110	6,0
3589(1)	G	33	59,7	18	13,6	100	4,0
3590	G	34	00	18	16	100	2,5
3591	G	34	00	18	18,1	78	1,5
3592	G	33	52	18	21,2	48	4,0
3593	G	33	53,9	18	26,8	10	1,0
CRUISE 300							
4634	G	30	27	17	14	129	3,0
4635	G	30	18	17	08,5	136	6,0

BEACH SAMPLES

STATION NO.	LATITUDE (SOUTH) degs.	mins.	LONGITUDE (EAST) degs.	mins.
1	33	45,1	18	26,1
2	33	11,0	18	09,0
3	33	08,3	17	58,0
4	32	58,0	17	52,0
5	32	59,0	17	52,0
6	32	48,6	17	52,0
7	32	43,5	17	56,0
8	32	46,4	18	01,5
9	32	47,2	18	06,5
10	32	41,3	18	14,0
11	32	37,0	18	17,0
12	32	29,7	18	19,0
13	32	24,0	18	18,9
14	32	17,1	18	20,0
15	32	10,5	18	18,0
16	32	03,0	18	17,2
17	31	55,5	18	16,0
18	31	48,9	18	13,1
19	31	44,8	18	12,0
20	31	42,5	18	11,4
21	31	30,8	18	02,0
22	31	24,1	17	55,0
23	31	14,8	17	49,5
24	31	07,0	17	43,1
25	30	58,0	17	38,0
26	30	51,8	17	33,8
27	30	41,3	17	27,5
28	30	37,5	17	25,0
29	30	19,3	17	16,0
30	33	34,5	18	19,0
31	33	54,0	18	20,0
32	34	01,4	18	19,0
33	34	10,0	18	20,4
36	34	20,5	19	00,0
37	34	02,4	18	20,9
39	34	02,4	18	20,8

RIVER SAMPLES

STATION NO.	LATITUDE (SOUTH) degs.	mins.	LONGITUDE (EAST) degs.	mins.
R- 1	32	47,2	18	09,1
2	32	19	18	21,8
3	31	33,7	18	25
4	31	12,6	17	53,6
5	31	02,4	17	45
6	30	46,3	17	37,2
7	30	34,7	17	29
8	30	25,2	17	26
9	30	13	17	19,5
10	30	21,7	17	30,5
11	30	49,0	18	06,9
12	31	23,5	18	39,4
13	31	29,1	18	42,4
14	31	37	18	42
15	31	41,5	18	30,6
16	31	52	18	40,8
17	32	05	18	49,5
18	32	22,1	18	56,0
19	32	34	18	59,3
20	32	57,9	18	43
21	32	59,5	18	21,9
23	32	19,6	19	31
24	32	18,5	19	34,5
25	32	43,4	19	02
31	31	45	18	35,8
32	31	33,9	18	19
33	31	41,5	18	11,2
34	30	35,1	17	58,7
36	30	32	17	53,3
37	33	49,9	18	29,7

APPENDIX II - METHODS AND RESULTS OF BASIC SEDIMENTOLOGICAL AND GEOCHEMICAL ANALYSES

II - A. Methods.

(i) Size analysis.

(ii) $CaCO_3$ determinations.

(iii) Organic carbon analysis.

(iv) K_2O and P_2O_5 determinations.

(v) An estimation of the faecal pellet content of the sediment.

II - B Results.

(i) Basic sedimentological data for all samples recovered from the Cape west coast.

On file at the University of Cape Town:-

(ii) Data derived from basic sedimentological parameters, including per cent organic matter, carbonate apatite; per cent glauconite, K_2O, organic carbon, organic matter and apatite all on a carbonate free basis as well as calcium carbonate corrected for the presence of carbonate apatite.

(iii) Particle-size determinations of the coarse fraction for selected samples.

(iv) Sand-sized component data for all samples.

II - A Methods

Interstitial salt was removed from all samples prior to mineralogical and geochemical analyses by dialysis.

Because several technicians were sometimes employed to carry out routine analyses, the amount of inter-operator error was established for the size determinations and for the organic carbon as well as for the calcium carbonate analyses. The analyst was not informed about these tests and handled the samples in the same manner as the routine sediment samples.

A(i) Size analysis.

Samples were wet-sieved through 63µm and 2 mm screens to separate the gravel and sand fractions from the mud (<63µm). The silt and clay contents were determined by pipetting using standard methods (Anonymous, 1967 and Rogers, 1971).

A total component size analysis was made of the sand-size fraction of 241 selected samples at half phi intervals. A particle-size and statistical analysis of the data was effected using a computer programme developed by R. Lefever, Department of Geology, University of California, Los Angeles and adapted for this study by G. Moir of the Geology Department, University of Cape Town.

The precision of the gravel/sand/silt/clay determinations was established for three operators for three sediments of markedly different textures (Table AII - 1 and Fig.AII-1). The precision with which each analyst worked was similar, except for determinations of the sand content of the faecal pellet mud which showed deviations of between 9 and 38%. This emphasizes the difficulties of aggregation and disaggregation when wet-sieving sediment containing a high faecal pellet content. Delicate foraminiferal tests easily break down during sieving and thus size determinations of these sediments, especially those from the deeper parts of the slope are also rather imprecise (5 to 10% deviations). The precision with which the remaining size determinations were made is a function of concentration. For example, the multiple analyses of glauconitic sand containing less than 5% silt and clay are relatively imprecise (deviations of between 15-20%), whereas foraminiferal and faecal pellet muds which contain approximately 30 and 40% silt and clay respectively, are more precise (deviating less than 6%) even although these sediments are more susceptible to disaggregation.

Two size analyses made by the Woods Hole Oceanographic Institution (WHOI), Boston, were similar to those obtained in this study (Table AII-1).

The methods used in dry-sieving the sand fractionhave been discussed in detail by Flemming (in prep.) and will not be considered here.

A(ii) $CaCO_3$ determinations.

The $CaCO_3$ content of the sediment was determined gasometrically (Hülsemann, 1966) and efficiency of the method as a sedimentological tool has been discussed in detail by Siesser and Rogers (1971).

Although the method is both accurate and precise (Table AII-1 and Fig.AII-2), highly imprecise data can be produced by inexperienced analysts (e.g. operator UCT(a) in Table AII-1). When duplicate analyses are considered it is clear that the analytical reliability is good (deviation <5%) for sediment containing more than 10% $CaCO_3$, but that precision deteriorates at lower $CaCO_3$ concentrations. High determinations made by WHOI, especially on the poorly calcareous samples is probably due to the method employed by that institution. This is evident from the high values produced for the analyses of artificial sediment containing 5% $CaCO_3$ (Table AII-1).

The coefficient of variation of the calcium carbonate determinations is less than 10% for all concentrations above 5% $CaCO_3$ and less than 20% for values less than this figure. The per cent deviation for the analyses of the artificial standards is less than 10% for all concentrations.

A(iii) Organic carbon analysis.

Organic carbon determinations were made by a standard wet chemical technique (Morgans, 1966). All non-oxidized carbon in the sediment is oxidized with hot chromic acid and the excess acid is titrated against ferrous sulphate. The method assumes that all the organic carbon in the sediment is in the same state of oxidation, thus it yields only approximate results. Emery (1960) found that organic carbon analyses obtained by back titration are consistentlyhigher, by a factor of 0,78, than those produced by dry combustion.

The variation in the precision with which different analysts work is high (deviations varied between 0 and 14%) for samples containing less than 2% organic carbon (Table AII-1 and Fig.AII-3). All analyses were made in duplicate and the deviation between a pair of results was less than 10% for samples containing more than 0,5% organic carbon. In this work it has been assumed that organic carbon levels of more than 1% and of less than 1% are characterized respectively by precisions of 15% and 30% at the 95% confidence level.

Summerhayes (1972) reports that mixtures of sucrose and quartz mixed in different proportions showed the method to be accurate within approximately 3% at the 95% confidence level for samples containing more than 1% organic carbon.

A(iv) K_2O and P_2O_5 determinations.

All K_2O determinations were made singleton by Phosphate Development Corporation (FOSKOR) Phalaborwa, Transvaal on a routine basis by X-ray fluorescence spectrometry (XRF). Duplicate analyses of 5 determinations show that the analytical precision of the method deteriorates slightly with decreasing

Table AII-1. Replicate analyses of geochemical and sedimentological techniques used in this investigation.

Size analyses (wet sieving)

Foraminiferal mud from slope(3117)

Analyst		Gravel	Sand	Silt	Clay
		0,0	20,2	32,8	47,0
A		0,0	19,2	34,4	46,4
		0,0	17,0	37,4	45,6
	$\bar{X}$	-	18,8	34,9	46,3
	Xpi	-	8,53	6,55	1,53
		0,0	20,1	34,3	45,6
B		0,0	22,4	32,9	44,7
		0,0	20,2	35,4	44,4
	$\bar{X}$	-	20,9	34,2	44,9
	Xpi	-	5,27	3,68	1,35
		0,0	21,7	32,5	45,8
C		0,0	20,5	31,7	47,8
		0,0	18,0	34,2	47,8
	$\bar{X}$	-	20,1	32,8	47,1
	Xpi	-	9,3	3,97	2,15
	$\bar{X}$ (total)		19,92	33,96	46,12
	P (total)		1,69	1,73	1,23
	R.D.(total)		3,46	5,09	2,67

Glauconitic sand from mid shelf(2441)

Analyst		Gravel	Sand	Silt	Clay
		0,0	93,8	2,2	4,0
A		0,0	93,6	2,3	4,0
		0,0	94,0	1,8	5,3
	$\bar{X}$	-	93,8	2,1	4,4
	Xpi	-	0,18	14,1	13,85
		0,0	93,1	2,5	4,4
B		0,0	93,8	2,2	4,0
		0,0	95,0	1,7	3,2
	$\bar{X}$	-	94,0	2,1	3,9
	Xpi	-	1,05	18,39	15,48
		0,0	92,5	2,4	5,1
C		0,0	94,0	1,8	4,2
		0,0	91,6	2,7	5,7
	$\bar{X}$	-	92,7	2,3	5,0
	Xpi	-	1,31	19,55	15,79

Table AII-1 (continued)

Analyst		Gravel	Sand	Silt	Clay
	$\bar{X}$(total)		93,33	2,22	4,43
	P(total)		1,20	,40	,87
	R.D.(total)		1,29	18,02	19,64

Nearshore Faecal Pellet Mud(2341)

Analyst		Gravel	Sand	Silt	Clay
		0,0	10,3	41,3	48,4
A		0,0	9,3	41,5	49,2
		0,0	14,9	38,0	41,2
	$\bar{X}$	-	11,5	40,3	46,3
	Xpi	-	22,83	4,43	2,09
		0,3	18,2	38,5	43,0
B		0,0	15,4	37,3	47,4
		0,0	15,3	37,3	47,4
	$\bar{X}$	-	16,3	37,7	45,9
	Xpi	-	8,58	1,58	4,85
		0,4	10,4	42,6	46,6
C		0,0	6,9	46,5	46,6
		0,5	4,8	46,9	49,8
	$\bar{X}$	-	7,4	45,3	47,7
	Xpi	-	36,83	4,78	1,46
	$\bar{X}$(total)		11,72	41,10	46,62
	P(total)		4,46	3,72	2,82
	R.D.(total)		38,05	9,05	6,05

Size analyses made at the University of Cape Town and at Woods Hole Oceanographic Institute.

	Sand		Silt		Clay	
Institution:	UCT	WHOI	UCT	WHOI	UCT	WHOI
Sample						
109	76	74	13	16	9	10
130	95	95	1	2	4	3

Table AII-1 (continued)

$CaCO_3$ determinations

Sediment samples

Analyst		1	2	3	4	5	6	7
		2,7	18,7	41,0	79,9	76,1	79,9	90,2
		3,3	17,5	40,8	80,1	74,0	78,9	91,1
U.C.T.(a)		2,8	18,5	42,8	81,3	73,8	78,5	90,7
	$\bar{X}$	2,9	18,2	41,5	80,4	74,6	79,1	90,7
	Xpi	10,0	3,31	2,39	0,87	1,53	0,88	0,49
		3,99	19,2	42,2	81,5	62,7	78,8	91,5
U.C.T.(b)		3,19	18,3	42,5	80,4	61,9	78,8	80,5
		2,80	18,9	40,9	78,2	77,6	77,9	90,0
		-	17,9	41,2	80,9	-	-	-
	$\bar{X}$	3,3	18,6	41,7	80,3	67,4	78,5	87,3
	Xpi	17,64	3,5	1,92	2,06	11,25	0,06	6,39
$\bar{X}$(total)		3,13	18,52	41,70	80,25	71,02	78,80	88,66
P(total)		0,48	0,59	0,90	1,19	6,90	0,65	4,60
R.D(total)		15,34	3,19	2,16	1,48	9,72	0,82	5,19
		8,1	23,2	53,0	84,7	78,1	83,0	93,6
WHOI		9,3	25,3	50,5	85,5	79,1	88,8	97,0
		9,4	27,1	-	85,3	-	83,9	-
	$\bar{X}$	8,9	25,2	51,8	85,2	78,6	85,2	95,3
	Xpi	7,43	7,75	2,41	0,47	0,95	3,37	1,78

Analyses of artificial sediment made by Woods Hole Oceanographic Institution and University of Cape Town (pure quartz and ANALAR $CaCO_3$)

Analyst		5%	10%	30%	50%	70%	90%
		4,2	10,2	28,4	50,4	68,2	87,6
U.C.T.		4,4	8,8	29,9	48,1	68,0	88,5
		4,5	8,6	26,3	47,4	69,2	85,7
	$\bar{X}$	4,4	9,2	28,2	48,6	68,5	87,3
	Xpi	3,45	8,51	6,40	3,06	0,87	1,60
		11,8	10,4	31,8	54,8	71,5	88,7
WHOI		5,7	10,7	29,8	50,3	70,5	91,1
		5,8	10,0	31,1	53,6	71,2	90,0
	$\bar{X}$	7,8	10,4	30,9	52,9	71,1	89,8
	Xpi	34,85	3,38	4,87	4,28	0,70	1,61

Table AII-1 (continued)

Organic carbon analyses

Analysts		Organic carbon samples 1	2	3	4	5
		,48	1,83	2,99	4,78	7,43
A		,54	1,89	2,99	4,72	7,63
		,46	1,85	2,98	4,68	7,52
	$\bar{X}$	,50	1,86	2,99	4,73	7,53
	Xpi	8,00	1,61	0,16	1,05	1,33
		,36	1,56	2,76	3,65	7,86
B		,36	2,04	2,79	3,65	7,81
		,36	1,88	2,82	3,97	8,01
	$\bar{X}$	,36	1,83	2,79	3,76	7,89
	Xpi	,00	13,33	1,07	4,20	1,26
		,23	1,57	2,58	3,85	6,66
C		,30	1,68	2,58	3,90	7,09
		,23	1,51	2,56	4,00	6,49
	$\bar{X}$	,25	1,58	2,57	3,92	6,75
	Xpi	13,20	5,33	0,39	1,91	4,42
	$\bar{X}$(total)	,37	1,75	2,77	4,13	7,39
	P(total)	,11	,18	,17	,46	,54
	R.D(total)	29,73	10,29	6,14	11,14	7,31

K_2O determinations (Phosphate Development Corporation)

	Samples 1	2	3	4	5
	1,27	2,23	2,41	4,09	4,91
	1,30	2,41	2,63	4,13	4,72
	1,26	2,43	2,45	3,86	5,12
	1,20	2,24	2,51	3,98	5,12
	1,29	2,12	2,48	4,01	5,00
$\bar{X}$	1,26	2,29	2,50	4,01	4,97
P	0,04	0,13	0,08	0,11	0,17
R.D.	3,17	5,68	3,20	2,74	3,42

Abbreviations:

$\bar{X}$ - mean value for each analyst

Xpi - percentage deviation for pair of values with the maximum variation for each analyst. $Xpi = \frac{xi - xii}{2} / \frac{xi + xii}{2}$ where xi and xii are the maximum and minimum values.

$\bar{X}$(total) - mean for all analysts.

P (total) - precision at the 95% confidence level for all analysts.

WHOI - Values obtained from Woods Hole Oceanographic Institution.

UCT - Values obtained in this study.

R.D. - Relative deviation $\left(\frac{P}{\bar{x}} \times \frac{100}{1}\right)$

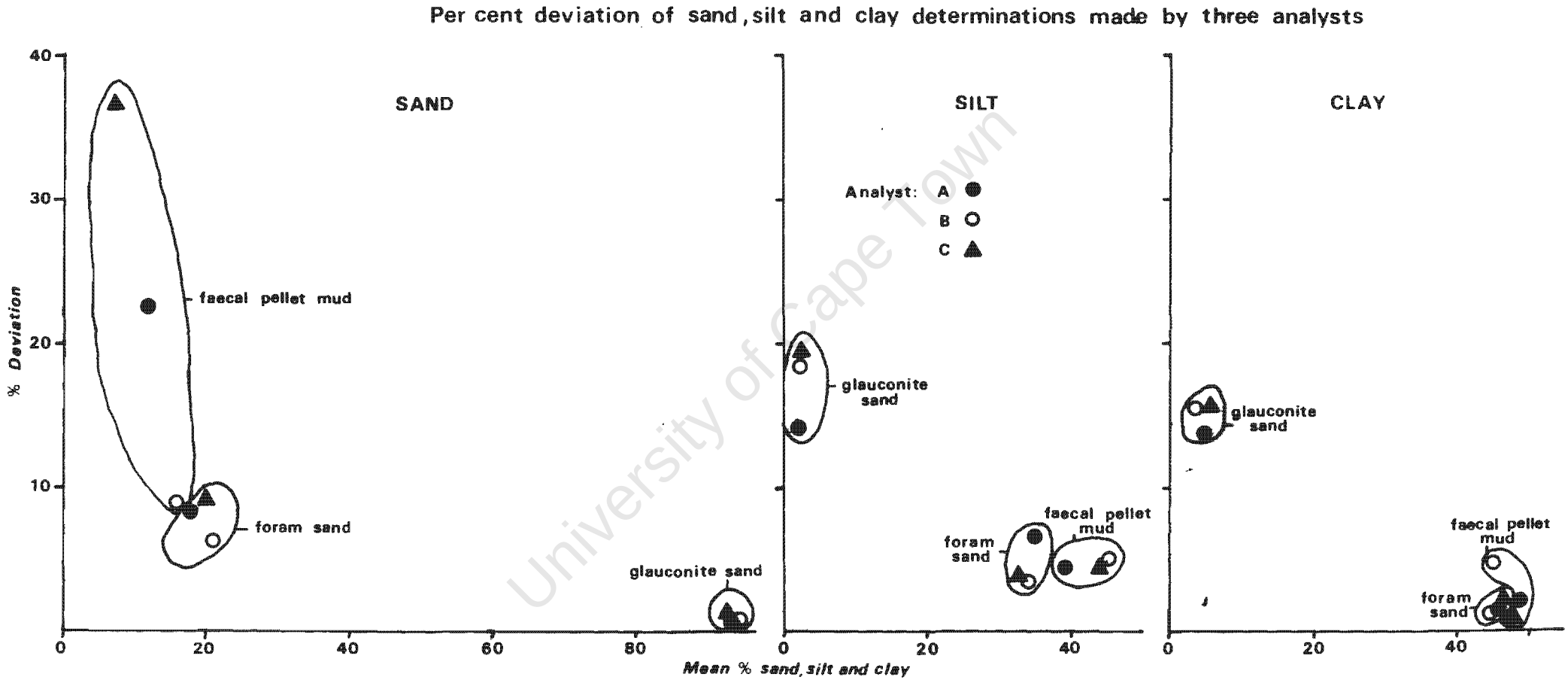
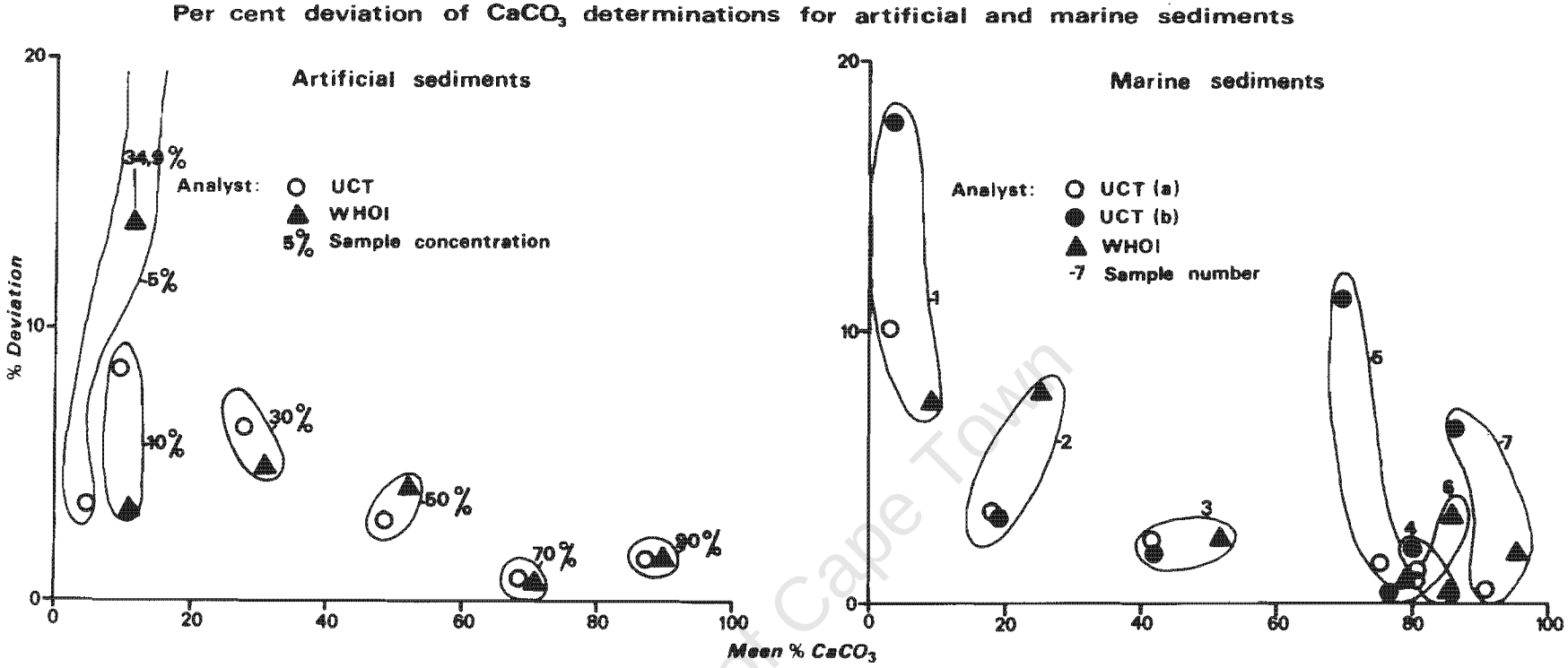


Figure AII-1



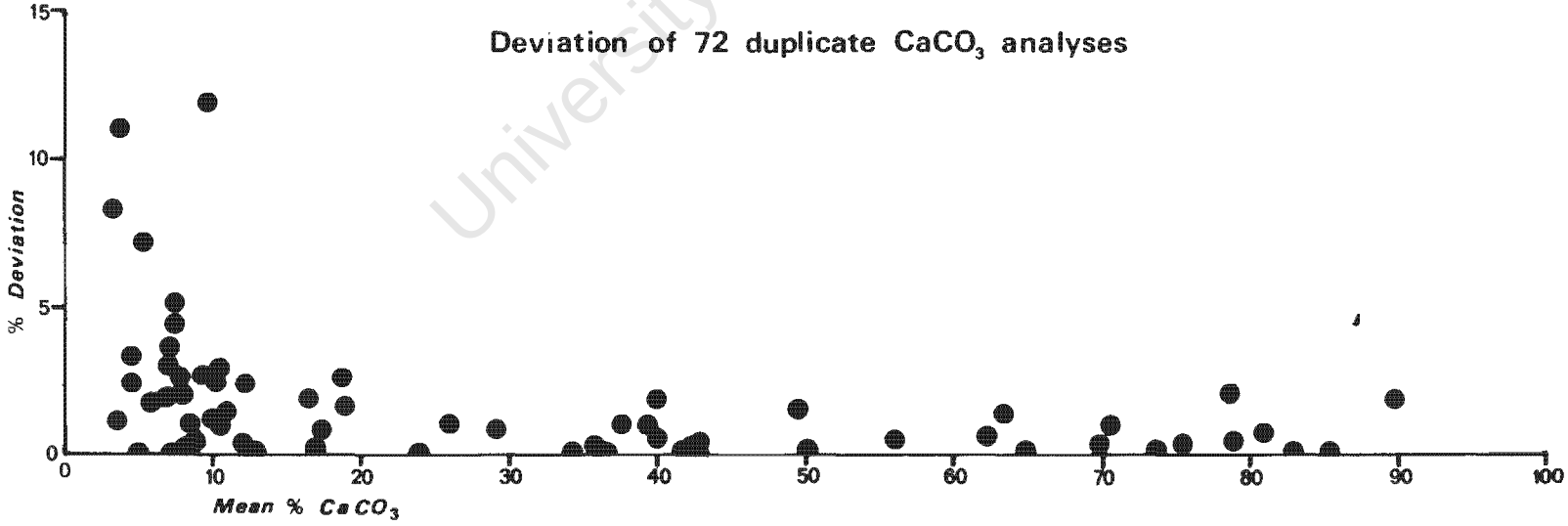


Figure AII-2

Per cent deviation of organic carbon determinations made by three analysts

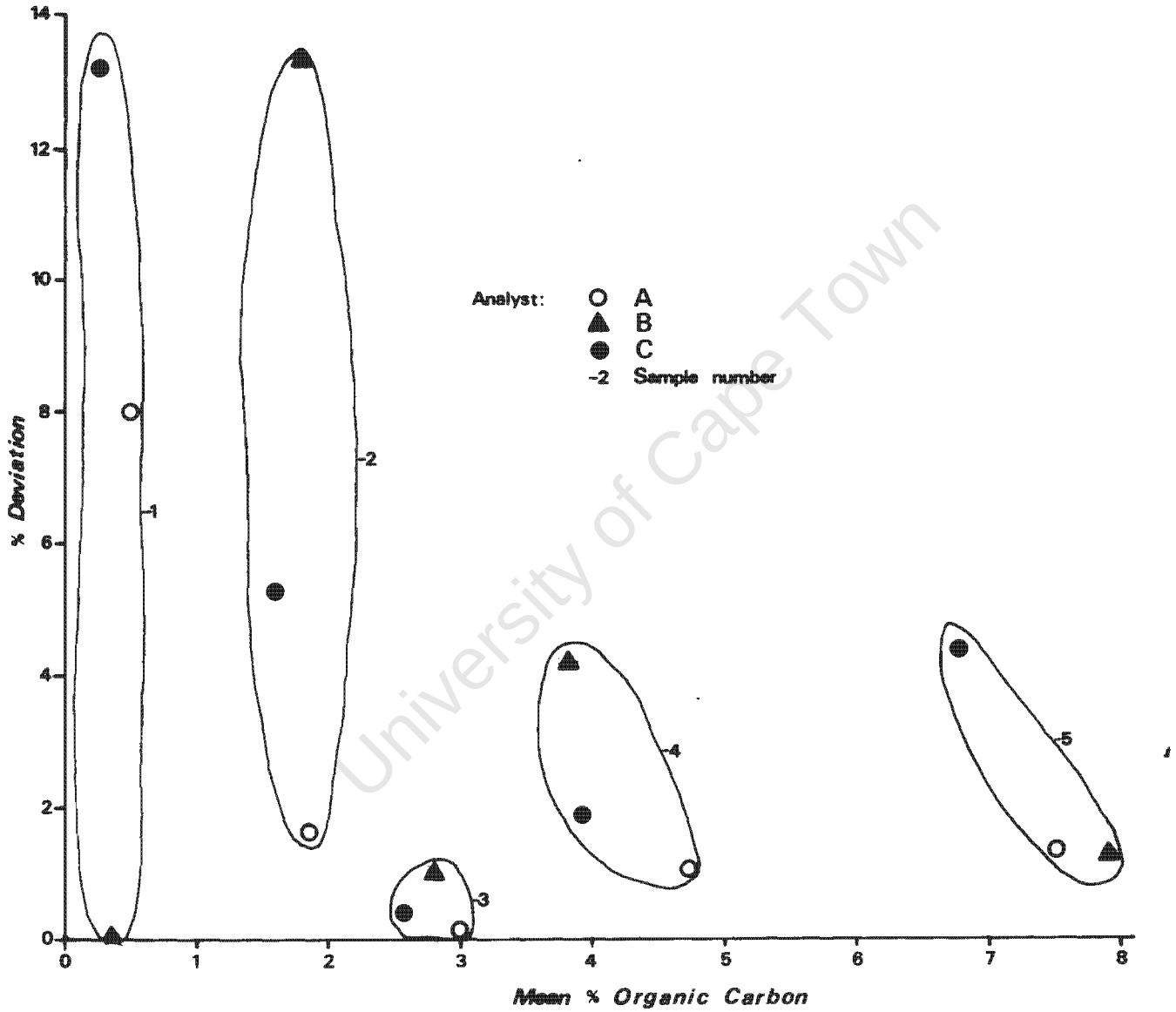


Figure AII-3

concentration. In this investigation the precision of the K_2O analyses at the 95% confidence level, is approximately 5% for all concentrations of K_2O.

Sub-samples were also routinely analysed for P_2O_5 by FOSKOR. Determinations were made spectrophotometrically using an ammonium vanadate-molybdate method having a standard deviation of 0,1, 0,4 and 0,5% at the 15, 5,0 and 0,5% P_2O_5 levels respectively and an accuracy of the same order (Summerhayes, 1972).

A(v) An estimation of the faecal pellet content of the sediment.

Faecal pellets may be considered as a sand-size component or texturally as part of the mud fraction, depending on the aspect of the study. In this investigation both aspects have been examined.

Faecal pellets vary from being very friable to partly indurated. The pellets can break down under gentle agitation in water during wet-sieving and may thus be erroneously included in the mud fraction or if more vigorous agitation is required, coarse, non-faecal pellet material may be disaggregated and included as part of the mud fraction. Thorough rewashing of the sand-size fraction during disaggregation procedures will produce additional fines, for example from within the tests of foraminifera or lodged in sutures of glauconite grains,which will be regarded as a faecal pellet component. Determination of the faecal pellet content is therefore a difficult procedure and all methods are likely to produce textural and/or compositional errors (see section (i)).

In an initial assessment of the faecal pellet content, pellets were soaked overnight in sodium hypochlorite and disaggregated by limited ultrasonic treatment. Although this method was satisfactory for quartzitic and glauconitic sands, less robust agglutinated benthic foraminifera in the near-shore muds and delicate, thin-walled planktonic foraminifera from the slope regions were also broken down by the ultrasonic treatment. A test made of foraminiferal sands which were devoid of faecal pellets produced faecal pellet values of up to 20% when this method was applied to these sediments.

Another disaggregation procedure was attempted by oxidizing the organic matter that binds the mud particles together. However, a check on this treatment made on faecal pellet-free foraminiferal sands resulted in faecal pellet values of 4-12%. The initial faecal pellet determinations have, therefore, been used in this study as an approximation of their concentration.

B(i). Basic sedimentological data for all samples recovered from the Cape west coast.

SAMPLE NO.	$CaCO_3$	P_2O_5	K_2O	GLAUCO-NITE	ORGANIC CARBON	GRAVEL	SAND	SILT	CLAY	FAECAL PELLETS	COLOUR
CRUISE 118											
100	15,9	1,7	2,45	21	1,4	0,00	87,4	4,9	7,8	10	10Y 6/2
101	2,0	2,0	2,28	25	0,4	0,01	97,7	0,1	3,1	0	10GY 6/2
102	14,0	5,1	5,40	69	0,5	0,07	96,0	0,8	3,2	0	5GY 5/2
103	10,5	5,4	3,51	69	0,6	0,26	90,1	3,5	6,2	0	5GY 5/2
104	14,8	5,2	4,73	66	1,0	0,26	92,1	3,7	4,0	0	5Y 6/2
105	17,9	4,5	4,76	46	0,9	0,04	86,2	8,2	5,5	0	5Y 5/4
106	20,9	1,3	1,85	11	1,3	0,00	83,6	8,8	7,6	0	5Y 5/4
108	23,8	1,0	1,54	3	1,6	0,00	74,2	16,1	9,7	0	5Y 6/4
109	18,7	1,5	2,01	15	1,2	0,00	75,5	13,4	9,4	0	5Y 6/2
110	20,9	4,6	5,25	54	1,0	0,00	84,3	9,2	6,6	0	10Y 6/2
111	16,3	4,5	3,86	64	0,5	0,06	92,0	3,0	5,0	0	5GY 5/2
112	7,4	5,0	1,61	65	0,7	0,10	92,7	0,8	6,4	0	5GY 5/2
113	1,9	1,8	4,31	48	0,2	0,10	93,2	6,7	5,5	0	5GY 5/2
CRUISE 121											
129	32,2	1,0	1,22	tr	2,2	0,00	66,9	15,8	17,3	10	5Y 5/2
130	3,5	2,0	2,36	27	0,3	0,22	94,7	0,6	4,5	0	5GY 5/2
131	7,4	2,6	2,45	27	0,5	0,00	92,2	2,3	5,5	0	10Y 6/2
135	16,0	2,5	2,30	27	0,7	0,23	91,8	2,4	5,6	0	10Y 6/2
136	17,0	5,0	3,31	58	0,5	0,06	93,1	1,8	5,1	0	5GY 5/2
CRUISE 123											
145	21,9	0,5	0,40	tr	0,2	14,08	85,8	0,1	0,0	0	N 7,5
147	11,4	1,2	2,14	10	1,2	0,01	73,8	11,9	14,3	1	N 7,5
149	71,3	2,5	2,30	tr	2,0	0,00	32,7	27,0	40,3	0	5Y 8/2
CRUISE 127											
168	11,1	0,4	0,51	tr	0,3	0,03	94,9	0,6	4,5	0	5Y 7/2
169	6,1	5,2	5,51	60	0,3	0,18	82,6	0,3	16,7	0	5GY 5/2
170	47,4	1,0	1,02	22	1,4	0,00	79,2	8,4	12,4	0	5Y 6/2
171	31,2	1,0	0,59	tr	0,6	0,49	90,5	3,1	5,9	0	5Y 7/2
172	52,3	0,2	1,20	tr	1,6	0,00	09,8	54,4	35,8	0	5Y 8/2
173	74,2	0,2	0,50	tr	0,5	0,00	10,7	44,4	44,9	0	5Y 8/2
174	14,2	1,2	1,94	12	0,9	0,00	77,8	09,6	12,7	0	10Y 6/2
175	17,8	5,1	1,25	58	0,4	0,00	92,3	2,7	5,0	0	5GY 7/2
176	8,7	2,2	5,05	53	0,3	1,04	91,9	1,8	5,2	0	10GY 5/2
177	35,8	1,4	1,95	16	0,7	1,10	89,6	3,5	5,9	0	5GY 7/2
178	25,4	2,9	5,10	8	1,0	0,00	84,6	8,5	6,9	0	5Y 5/4
179	78,3	0,1	0,50	0	0,5	0,00	12,7	29,4	57,9	0	5YR 8/1

SAMPLE NO.	$CaCO_3$	P_2O_5	K_2O	GLAUCO-NITE	ORGANIC CARBON	GRAVEL	SAND	SILT	CLAY	FAECAL PELLETS	COLOUR
CRUISE 131											
200	20,6	0,5	0,90	tr	0,8	0,09	91,7	3,2	5,1	0	10Y 6/2
201	16,9	1,0	1,69	5	2,3	0,06	62,6	17,3	20,1	5	N 7,5
202	8,6	1,0	5,00	61	0,2	0,00	91,3	4,7	4,0	0	5GY 5/2
204	71,1	0,3	0,77	0	0,7	0,00	11,8	40,2	48,0	0	5YR 8/1
205	53,8	1,1	2,60	13	1,1	0,00	55,9	29,1	15,1	1	5Y 8/2
206	32,4	3,2	4,19	19	1,4	0,04	62,7	21,6	15,6	0	10Y 6/2
207	10,6	5,0	6,38	76	0,4	0,34	92,4	1,9	5,3	0	5GY 5/2
208	6,3	2,0	2,30	10	1,7	0,00	76,3	10,0	13,7	7	5Y 5/2
209	3,9	1,1	4,77	35	1,2	0,00	80,1	8,1	11,8	2	5GY 4/2
210	3,0	0,7	1,50	3	0,1	0,00	82,6	9,1	8,4	0	5Y 8/1
CRUISE 142											
264	38,8	0,6	1,20	4	0,6	5,30	84,5	5,1	5,1	0	10GY 5/2
265	81,2	0,2	0,52	tr	0,5	2,10	91,0	0,5	6,5	0	5Y 8/1
266	61,1	0,3	0,59	tr	1,4	13,10	72,5	5,6	8,8	0	10Y 7/2
269	47,8	1,0	1,30	tr	3,7	0,20	54,1	23,6	22,1	12	5Y 6/2
270	46,5	0,3	1,14	tr	3,8	0,00	47,5	29,7	22,9	20	5Y 6/2
271	91,1	0,1	0,24	tr	0,3	59,00	34,9	0,1	5,5	0	N 8
CRUISE 146											
286	5,1	2,0	5,25	56	0,4	0,40	95,2	0,6	3,0	0	10GY 5/2
287	15,9	5,0	1,63	73	0,4	0,50	90,7	3,2	5,6	0	5GY 5/2
288	52,9	0,2	1,20	tr	1,7	0,00	05,9	26,8	67,3	0	5Y 8/2
290	25,2	6,0	1,37	65	0,4	0,81	94,6	1,3	4,2	0	5GY 7/2
292	41,9	6,8	2,01	12	0,8	23,30	52,2	12,1	12,1	0	10Y 7/2
295	20,6	5,9	3,74	3	1,5	1,10	88,6	1,2	9,2	0	5GY 7/2
296	49,3	0,8	0,93	3	1,4	0,03	81,4	8,7	9,9	0	5Y 6/2
297	59,0	0,8	1,25	2	2,6	0,00	58,1	21,3	20,7	12	5Y 6/2
298	41,5	0,6	1,44	tr	4,1	0,41	49,5	25,7	24,5	16	5Y 6/2
299	56,6	1,1	0,95	tr	1,5	0,18	71,8	14,9	13,2	0	5Y 6/2
300	36,5	1,1	1,08	3	1,2	0,08	82,3	7,9	9,7	0	5Y 6/2
308	35,6	0,3	1,56	tr	2,3	0,07	37,0	31,1	31,1	1	5Y 6/2
309	40,5	0,3	1,21	tr	2,2	0,00	45,5	35,9	18,6	0	5Y 6/2
311	37,9	1,3	1,41	10	0,8	2,90	86,6	3,8	6,8	0	10Y 7/2
312	8,3	1,9	6,08	63	0,4	0,30	95,0	0,9	3,8	0	5GY 5/2
CRUISE 148											
330	72,8	0,5	0,76	tr	1,5	0,20	69,5	15,1	15,3	0	5Y 6/4
331	52,9	0,5	1,36	4	3,0	0,04	60,5	20,5	19,2	17	5Y 5/4

SAMPLE NO.	$CaCO_3$	P_2O_5	K_2O	GLAUCO-NITE	ORGANIC CARBON	GRAVEL	SAND	SILT	CLAY	FAECAL PELLETS	COLOUR
CRUISE 148 contd.											
332	43,1	0,3	1,44	tr	4,2	0,14	41,0	30,9	28,0	10	5Y 6/2
335	51,9	0,5	0,88	0	2,7	0,00	55,7	23,0	21,0	12	5Y 6/2
CRUISE 187											
833	36,2	0,4	0,68	tr	0,8	0,20	89,8	4,7	5,3	0	5Y 7/2
CRUISE 219											
1675	72,9	0,8	0,80	tr	1,5	0,01	75,1	14,0	11,0	2	5Y 6/2
1686	42,2	0,5	1,50	tr	4,3	0,09	46,8	26,1	27,1	42	5Y 6/2
1687	63,6	4,0	0,97	tr	2,9	0,05	61,4	22,9	15,7	12	5Y 6/2
1688	61,7	1,3	0,73	tr	1,5	0,04	73,5	14,0	12,4	6	5Y 6/2
1689	44,5	1,4	1,10	tr	2,1	0,05	72,3	16,5	11,1	4	N 7,5
1690	48,1	0,4	1,07	tr	3,5	0,00	58,9	15,8	25,2	32	N 7,5
1691	41,9	0,1	0,95	tr	0,7	0,44	91,6	3,5	4,4	0	10Y 7/2
1692	10,7	2,1	2,92	56	0,5	0,05	93,2	1,9	4,8	0	5GY 5/2
1693	14,0	2,6	3,20	49	0,6	0,00	91,4	3,9	5,5	0	5Y 8/2
1694	23,7	1,7	5,58	38	0,8	0,02	96,1	4,4	5,9	0	10Y 5/2
1695	20,3	1,5	3,40	33	0,6	0,07	90,8	2,0	7,1	0	5GY 7/2
1696	20,0	1,7	5,00	54	0,9	0,13	86,4	5,5	7,9	0	5GY 5/2
1697	15,2	2,8	4,00	32	0,8	2,10	78,7	8,4	10,5	0	10Y 6/2
1698	20,6	1,7	3,80	41	0,8	0,29	82,3	8,4	9,0	0	10Y 5/2
1699	26,7	3,3	3,3	30	1,1	1,57	74,8	10,2	13,5	0	10Y 6/2
1700	37,7	6,4	2,23	34	0,7	4,70	86,4	1,6	7,3	0	5GY 7/2
1701	23,7	0,9	2,38	63	0,4	i s	i s	i s	i s	0	10GY 6/2
1702	35,9	1,9	1,90	15	0,6	1,34	85,7	2,5	10,5	0	10Y 7/2
1705	10,6	3,9	5,60	64	0,5	0,40	91,2	2,6	5,8	0	5GY 5/2
1710	10,4	2,4	5,70	65	0,2	0,63	87,4	8,4	3,6	0	5GY 5/2
1711	2,4	1,5	4,50	54	0,3	0,06	95,0	1,0	4,0	0	10GY 5/2
1713	6,9	1,4	1,69	16	0,4	0,17	93,3	0,9	5,7	0	10Y 5/2
1714	9,8	5,0	3,15	70	0,7	0,15	91,7	0,8	7,4	0	10Y 5/2
1715	16,1	4,7	3,88	44	0,9	0,00	87,3	7,7	4,9	0	10Y 6/2
1717	5,3	2,8	4,40	49	0,5	0,00	92,7	3,8	3,5	0	5GY 5/2
1718	5,5	1,8	2,52	25	0,7	0,00	90,8	4,7	4,5	0	10Y 6/2
1719	5,5	2,1	1,96	30	0,8	0,00	93,2	3,5	3,3	0	5GY 5/2
1720	18,2	1,4	1,81	14	1,4	0,00	81,6	7,7	10,7	23	10Y 6/2
1721	56,8	0,3	0,90	tr	1,6	8,90	72,0	11,3	7,8	0	10Y 7/2
CRUISE 236											
2203	33,5	0,4	1,24	tr	3,0	0,00	56,6	25,2	18,2	0	10Y 6/2

SAMPLE NO.	$CaCO_3$	P_2O_5	K_2O	GLAUCO-NITE	ORGANIC CARBON	GRAVEL	SAND	SILT	CLAY	FAECAL PELLETS	COLOUR
CRUISE 236 contd.											
2205	17,2	0,8	1.52	tr	1,5	0,00	84,0	9,0	7,0	4	5Y 5/2
2206	10,0	1,7	1,78	15	1,1	0,00	89,0	6,7	4,4	9	5GY 4/2
2207	24,0	0,5	1,14	tr	1,5	0,04	75,4	13,0	11,7	6	N 7,5
2209	62,3	0,7	0,65	0	0,3	10,40	88,5	0,4	0,7	0	N 8
2211	10,3	0,6	0,33	tr	0,1	0,63	97,9	0,3	2,7	0	5Y 8/1
2221	5,0	0,5	2,52	15	1,6	0,20	73,4	7,6	18,9	3	5GY 4/2
2222	7,3	1,0	2,81	5	2,4	0,00	70,7	9,7	19,6	9	N 7,5
2224	40,1	0,7	0,46	tr	0,4	0,82	95,9	0,9	1,2	0	N 7,5
2227	13,4	0,3	1,74	tr	3,7	0,01	56,6	22,7	20,8	6	N 7,5
2228	8,7	0,7	2,76	9	3,0	0,00	67,6	14,2	18,1	10	5Y 5/2
2229	2,6	1,4	2,85	27	0,6	0,30	86,8	2,0	10,9	0	10Y 4/2
2233	45,2	0,7	1,15	4	1,5	0,03	50,7	27,1	22,1	0	5Y 7/2
2237	6,1	0,3	1,36	3	2,3	0,43	70,3	8,7	20,6	10	5Y 5/2
2238	6,4	1,0	1,75	13	1,9	2,10	70,6	5,9	21,4	9	5GY 4/2
2239	3,4	1,7	4,70	49	0,7	0,31	89,9	1,1	8,7	0	5GY 5/2
2240	26,3	5,8	4,12	58	0,8	0,00	88,1	3,8	8,1	0	5GY 7/2
2241	17,4	5,0	5,87	65	1,0	0,66	84,5	3,8	8,4	0	5GY 5/2
2242	50,2	0,4	1,15	tr	4,0	0,00	26,1	35,6	38,3	10	N 7,5
2243	43,8	1,0	2,01	12	1,6	0,00	45,9	38,8	25,3	14	5Y 6/2
2244	30,8	3,0	4,31	37	1,7	0,00	69,1	10,3	20,6	21	10Y 6/2
2245	5,2	5,0	7,40	88	0,5	0,50	91,4	1,5	6,6	0	5GY 5/2
2246	7,8	5,2	6,86	78	0,5	6,20	86,1	1,7	6,1	0	5GY 5/2
2247	10,9	7,3	6,92	79	0,4	0,12	92,5	5,7	1,8	0	5GY 5/2
2248	6,4	6,3	3,70	46	0,7	6,30	84,4	4,0	5,2	0	5GY 5/2
2249	19,1	6,8	4,48	48	0,8	18,34	72,2	2,0	7,5	0	5GY 5/2
2251	5,2	0,4	1,40	tr	1,9	0,12	56,6	15,3	27,9	7	5Y 5/2
2252	3,5	0,8	1,47	5	0,9	0,00	82,1	3,0	14,9	4	10GY 6/2
2253	1,9	1,0	4,22	47	0,4	0,00	88,4	2,4	9,2	0	5GY 5/2
2254	20,9	4,7	4,20	54	0,9	0,00	86,7	3,5	9,8	0	10Y 6/2
2257	7,2	0,4	1,90	tr	4,4	0,22	59,8	17,1	22,9	17	5Y 5/2
2258	4,4	1,2	2,20	2	1,3	1,00	81,0	5,0	14,0	2	5Y 4/4
2259	7,2	6,2	6,60	83	0,7	0,00	91,0	3,1	5,9	0	5GY 5/2
2260	7,9	1,8	6,80	79	0,8	0,00	89,3	2,8	7,9	0	10GY 5/2
2262	4,9	0,9	1,97	3	1,4	0,00	41,7	26,8	31,5	17	5GY 4/2
2264	24,4	0,6	1,15	tr	1,3	0,00	76,1	3,8	20,1	0	5Y 7/2
2265	29,9	0,8	1,68	tr	2,8	0,00	51,0	21,2	27,8	16	N 7,5

SAMPLE NO.	$CaCO_3$	P_2O_5	K_2O	GLAUCO-NITE	ORGANIC CARBON	GRAVEL	SAND	SILT	CLAY	FAECAL PELLETS	COLOUR
CRUISE 236 contd.											
2267	5,8	4,0	6,07	68	0,7	0,30	84,4	4,6	10,7	0	5GY 5/2
2268	7,8	4,6	5,04	63	0,9	0,00	87,0	4,5	8,6	2	5GY 4/2
2269	7,9	3,7	3,38	37	0,9	0,00	90,2	5,0	5,6	2	5GY 4/2
2270	5,5	5,3	2,08	18	0,6	0,00	87,9	1,0	11,2	0	5GY 4/2
2271	10,7	1,8	3,43	28	3,6	0,00	55,2	29,2	15,5	12	5Y 5/2
2272	5,8	0,2	1,17	tr	2,4	0,80	66,7	10,7	21,8	9	N 7,5
2273	1,6	0,2	0,61	0	1,0	0,00	67,8	11,1	21,2	8	5Y 4/4
2274	40,6	0,3	1,07	0	3,0	28,70	42,4	7,1	21,7	26	5Y 7/2
2275	35,6	0,2	0,29	0	0,2	27,40	64,3	0,6	7,7	0	5Y 8/1
2276	13,9	0,2	0,31	0	0,2	0,00	94,6	2,0	3,4	0	5Y 8/1
2277	7,0	0,4	2,51	0	7,3	0,20	37,4	22,4	40,0	6	5Y 4/4
2278	4,2	0,4	1,48	tr	2,8	0,20	61,4	13,9	24,4	35	5Y 4/4
2279	19,8	0,6	2,03	tr	6,0	0,00	51,7	18,6	29,7	23	5Y 5/2
2280	8,0	0,8	1,17	tr	1,1	0,10	85,5	4,5	9,8	4	N 7,5
2281	9,4	0,9	1,23	2	1,3	0,00	82,1	4,8	11,9	2	10Y 5/2
2282	7,7	3,1	4,18	37	1,2	0,00	79,2	6,6	14,2	4	10Y 5/2
2283	14,0	2,4	4,00	33	1,5	0,00	72,6	11,4	15,9	0	10Y 5/2
2284	33,2	1,1	1,70	11	1,3	0,00	74,6	6,6	18,7	0	N 7,5
2286	33,9	0,6	1,70	tr	1,7	0,00	74,8	13,8	11,4	0	5Y 7/2
2287	18,8	0,7	1,50	tr	1,2	0,00	69,1	20,1	10,8	0	5Y 6/2
2288	20,0	0,4	1,20	tr	1,8	0,00	62,7	19,9	17,5	2	N 7,5
2289	14,6	0,5	1,10	tr	1,7	0,00	74,2	12,4	13,4	4	N 7,5
2290	12,3	0,5	1,00	tr	1,7	0,00	69,8	13,8	16,4	5	N 7,5
2291	9,9	0,5	1,10	tr	1,7	0,07	80,8	7,3	11,8	24	5Y 5/2
2292	1,8	0,5	1,50	tr	2,3	0,00	72,9	10,4	16,7	14	5Y 5/2
2293	5,8	0,4	1,20	tr	2,0	0,00	74,3	8,1	17,6	12	5Y 4/4
2294	8,6	0,4	1,70	tr	5,3	0,00	57,8	16,1	32,1	17	5Y 4/4
2295	5,0	0,3	2,80	tr	6,7	2,80	37,0	14,6	45,6	38	5Y 5/2
CRUISE 239											
2326	1,8	0,3	1,91	0	0,4	6,20	86,9	4,1	02,8	0	5Y 8/1
2328	3,1	1,8	3,00	tr	4,3	0,00	01,3	18,3	80,3	0	5Y 8/1
2329	7,2	0,6	1,60	tr	4,8	0,00	39,0	20,7	40,3	14	5Y 4/4
2330	4,7	0,6	1,20	tr	1,9	0,00	77,2	7,4	15,4	9	5Y 4/4
2331	4,7	0,6	1,3	tr	1,5	0,00	80,5	6,9	12,6	7	5Y 4/4
2332	7,3	0,5	1,60	tr	1,7	0,00	78,1	9,4	12,5	7	5Y 5/2

SAMPLE NO.	$CaCO_3$	P_2O_5	K_2O	GLAUCO-NITE	ORGANIC CARBON	GRAVEL	SAND	SILT	CLAY	FAECAL PELLETS	COLOUR
CRUISE 239 contd.											
2333	12,8	0,3	1,20	tr	2,0	0,00	72,3	12,8	14,9	9	5Y 5/2
2335	19,8	0,4	1,40	tr	2,5	0,70	47,0	28,1	24,1	3	N 7,5
2336	9,0	0,3	1,20	tr	1,7	0,00	75,5	12,0	12,5	8	5Y 5/2
2337	6,7	0,4	1,20	tr	2,3	0,00	77,1	10,6	12,3	12	5Y 5/2
2338	6,5	0,4	1,30	tr	2,6	0,00	69,1	13,0	17,9	12	5Y 4/4
2339	6,8	4,3	1,50	tr	4,0	0,00	68,8	11,4	18,6	25	5Y 4/4
2340	8,5	0,3	2,10	tr	4,5	0,00	46,0	17,6	36,4	39	5Y 6/2
2341	5,0	0,3	2,90	0	3,5	0,00	08,0	38,7	53,3	7	5Y 7/2
2342	7,2	0,2	2,60	0	1,9	0,00	19,8	38,3	41,9	11	5Y 7/2
2343	8,9	0,5	2,40	tr	7,3	0,00	26,6	25,2	48,1	26	5Y 5/2
2344	5,2	0,3	1,60	tr	4,8	0,00	68,9	16,6	14,5	36	5Y 4/4
2345	12,0	0,4	1,99	tr	5,5	0,00	63,6	17,5	19,0	13	5Y 4/4
2346	14,2	0,3	1,07	tr	1,9	4,80	76,0	11,0	8,3	9	5Y 5/2
2348	28,1	0,4	1,15	tr	3,6	0,00	62,4	25,5	12,2	15	N 7,5
2349	69,3	2,4	0,93	7	1,8	0,42	82,8	13,0	4,6	0	5Y 7/2
2350	29,7	0,6	0,89	tr	1,7	0,00	78,1	10,9	11,0	2	5Y 6/2
2352	10,5	0,3	1,41	tr	6,3	0,00	38,1	29,6	32,3	38	5Y 4/4
2353	9,4	0,3	2,30	0	5,9	0,00	36,1	31,3	32,6	35	5Y 4/4
2354	8,3	0,2	2,30	0	5,6	0,00	48,2	27,9	24,0	38	5Y 5/2
2355	0,6	0,8	0,57	0	0,2	2,10	93,5	0,5	3,9	0	5Y 5/2
2356	8,2	0,3	2,50	tr	6,9	0,00	57,0	19,6	23,5	56	5Y 5/2
2357	8,6	0,7	2,00	tr	7,4	0,00	51,7	18,3	30,0	51	5Y 4/4
2358	11,9	0,8	1,70	tr	5,6	0,00	68,7	13,7	17,6	54	5Y 4/4
2359	9,7	0,3	1,00	tr	2,9	0,00	74,4	11,3	14,3	16	5Y 5/2
2360	17,8	0,3	1,30	tr	3,1	0,00	64,5	18,7	16,7	14	5Y 5/2
2361	80,3	0,5	0,61	4	1,4	3,80	74,4	8,6	13,2	0	5Y 6/2
2362	56,4	2,4	2,40	31	1,9	1,00	86,1	3,3	9,6	3	5Y 6/2
2363	14,9	1,6	0,80	3	1,1	0,00	83,9	6,6	9,6	8	5Y 6/2
2364	12,7	1,6	1,10	tr	2,4	0,00	72,4	11,1	16,5	12	5Y 5/2
2365	8,0	0,4	2,20	tr	5,8	0,00	40,4	26,3	33,3	39	5Y 5/2
2366	10,3	0,3	1,80	tr	4,3	0,00	56,4	16,2	27,4	36	5Y 5/2
2367	5,9	0,4	1,40	tr	3,4	0,00	49,5	20,8	29,7	20	5Y 5/2
2368	7,3	0,7	1,40	tr	1,1	1,02	60,0	20,2	18,8	12	5Y 6/2
2369	29,9	0,8	0,79	3	1,3	0,00	81,9	7,3	10,8	4	5Y 6/2
2370	14,6	0,7	0,92	tr	1,3	0,00	84,2	6,7	9,1	3	5Y 5/2

SAMPLE NO.	$CaCO_3$	P_2O_5	K_2O	GLAUCO-NITE	ORGANIC CARBON	GRAVEL	SAND	SILT	CLAY	FAECAL PELLETS	COLOUR
CRUISE 239 contd.											
2371	42,8	1,4	1,28	11	1,7	0,00	77,1	9,4	13,4	2	5Y 6/2
2372	42,2	1,6	1,83	32	1,3	0,00	80,7	8,5	10,8	3	5Y 6/2
2373	70,2	1,0	0,65	5	1,6	0,30	78,3	9,2	12,2	2	5Y 6/4
2374	35,3	1,9	2,10	22	2,2	0,00	75,1	13,6	11,3	5	5Y 6/2
2375	25,9	0,5	0,95	tr	2,2	0,00	73,3	13,7	12,1	14	N 7,5
2376	15,0	0,6	0,92	tr	1,7	0,00	76,4	8,9	14,8	12	5Y 5/2
2377	11,1	0,5	1,30	tr	1,9	0,00	74,1	10,7	15,2	13	5Y 5/2
2378	9,3	0,3	2,00	tr	4,3	0,00	35,7	29,4	34,8	35	5Y 4/4
2381	4,3	0,5	1,70	tr	1,8	0,00	63,1	13,2	22,8	7	5Y 4/4
2382	42,8	0,4	1,58	tr	2,6	0,00	70,5	17,1	11,5	31	5Y 6/2
2383	12,2	0,9	0,67	tr	1,9	22,01	56,9	5,7	15,3	0	5Y 6/2
CRUISE 244											
2432	2,3	2,7	2,90	36	0,3	0,00	97,7	1,2	1,0	0	N 7,5
2433	3,1	3,3	3,48	41	0,4	0,11	78,5	1,1	20,4	0	5GY 5/2
2434	40,0	4,7	3,79	7	0,4	6,23	61,1	20,3	12,3	0	N 8
2435	14,2	2,9	3,47	35	0,8	0,00	85,8	5,8	8,4	0	5GY 5/2
2436	12,1	1,1	1,77	8	0,7	0,00	74,7	9,4	15,1	6	10Y 6/2
2437	8,0	1,2	1,79	4	1,2	0,10	42,6	36,9	20,4	2	5Y 6/2
2438	10,4	5,0	4,36	18	0,6	0,08	80,0	6,5	13,6	2	10Y 6/2
2439	6,0	0,5	i s	31	0,5	-	-	-	-	2	10Y 6/2
2440	39,8	2,3	4,00	46	1,3	0,00	76,1	13,7	9,3	4	10Y 6/2
2441	21,6	0,8	2,40	27	0,6	0,00	95,7	1,4	2,9	8	10GY 6/2
2442	9,7	5,1	6,10	80	1,5	0,00	90,3	3,7	5,9	3	10GY 5/2
2443	6,0	4,5	7,10	86	0,7	0,00	91,2	3,2	5,6	4	5GY 5/2
2444	19,6	3,0	4,90	49	1,5	0,00	74,7	8,2	17,1	5	5Y 6/2
2445	22,6	0,5	1,21	tr	1,9	0,00	69,4	16,8	13,7	4	5Y 7/2
2446	36,7	1,9	2,64	24	1,3	0,00	75,5	12,1	11,6	0	5Y 7/2
2447	55,6	2,0	2,32	22	1,3	0,00	77,0	11,1	11,8	0	5Y 7/4
2448	48,1	1,6	1,50	16	1,0	0,00	79,5	14,2	6,3	0	10Y 6/2
2450	46,0	2,8	3,50	43	0,9	0,00	93,5	5,7	0,8	0	10Y 6/2
2451	40,0	2,3	4,86	53	0,7	0,10	91,4	5,0	3,5	0	10Y 7/2
2452	37,9	1,3	1,89	17	2,3	0,00	72,6	19,6	7,8	1	5Y 6/2
2453	15,1	0,4	1,39	tr	1,3	0,00	71,4	14,8	13,9	13	N 7,5
2454	58,0	0,8	2,46	4	1,6	0,00	77,7	10,5	11,9	0	5Y 7/2
2455	70,8	3,6	1,60	26	1,6	0,00	79,8	10,3	9,9	0	5Y 6/4

SAMPLE NO.	$CaCO_3$	P_2O_5	K_2O	GLAUCO-NITE	ORGANIC CARBON	GRAVEL	SAND	SILT	CLAY	FAECAL PELLETS	COLOUR
CRUISE 244 contd.											
2456	49,1	1,5	4,06	9	1,2	1,60	72,6	12,0	13,9	4	10GY 5/2
2457	29,0	2,8	2,83	35	1,3	0,00	81,9	8,6	9,8	0	5Y 6/2
2458	37,4	4,3	1,26	43	0,6	i s	i s	i s	i s	0	5GY 5/2
2459	69,8	4,3	1,04	8	0,9	0,00	84,8	6,1	9,1	0	5Y 6/4
2460	73,4	0,5	0,79	3	2,0	4,20	67,4	11,6	16,8	0	5Y 6/4
2461	45,3	4,5	3,15	39	0,9	0,00	85,8	6,0	8,2	0	5Y 6/4
2462	69,1	3,3	1,24	11	0,9	i s	i s	i s	i s	0	10Y 7/2
2463	87,2	1,5	0,70	2	1,5	0,00	80,9	9,9	9,3	0	5Y 6/4
2464	79,9	3,4	0,56	7	1,0	0,00	85,3	7,5	7,1	0	5Y 7/4
2465	80,0	5,3	0,20	7	0,8	0,00	89,8	7,0	3,1	0	5Y 7/2
2466	87,0	1,1	0,3	tr	0,8	0,00	92,3	6,2	1,5	0	5Y 6/4
2467	89,7	1,0	0,25	0	1,4	0,00	80,8	11,0	8,2	0	5Y 6/4
2470	88,2	0,5	1,26	tr	1,9	0,00	73,4	13,1	13,6	0	5Y 5/4
2471	86,8	0,5	0,68	tr	0,8	0,60	87,8	4,9	6,7	0	5Y 8/2
2472	92,9	0,4	0,16	tr	0,9	0,00	86,4	8,2	5,4	0	5Y 7/2
2473	90,0	0,9	0,18	tr	0,7	1,00	88,6	5,8	4,6	0	5Y 7/2
2474	87,1	0,7	0,36	tr	1,2	0,50	80,3	1,3	17,9	0	5Y 5/4
2475	76,6	1,3	0,73	6	1,6	1,40	76,9	6,3	15,3	2	5Y 5/4
2476	47,6	1,0	1,28	7	2,5	0,00	66,8	13,7	19,4	3	5Y 6/2
2477	26,3	0,4	0,94	tr	1,3	0,00	70,3	12,5	17,2	12	5Y 6/2
2478	21,2	0,6	1,11	tr	1,5	0,00	65,8	14,1	19,2	13	5Y 5/2
2479	10,4	0,3	2,04	0	4,4	0,00	40,1	26,7	33,3	37	5Y 4/4
2480	6,6	0,4	2,10	0	3,9	0,00	36,4	28,1	38,5	31	5Y 4/4
2482	13,3	0,6	0,98	tr	1,0	0,00	81,2	6,9	11,8	4	5Y 6/2
2483	71,7	2,4	0,39	5	1,1	0,00	75,8	11,9	12,3	3	5Y 6/4
2484	84,3	1,0	0,39	2	1,2	0,00	76,8	10,7	12,5	0	5Y 7/4
2485	91,2	0,5	0,18	tr	0,8	0,00	80,4	7,4	12,2	0	5Y 7/2
2486	89,7	0,4	0,16	tr	0,8	0,00	70,9	2,8	26,3	0	5Y 7/2
2488	84,3	0,3	0,44	0	3,0	0,00	55,8	25,2	19,0	0	5Y 7/2
2489	80,0	0,4	0,37	tr	2,6	0,00	65,3	21,9	12,8	7	5Y 6/4
2490	44,5	2,1	0,89	8	1,8	0,00	77,4	11,5	11,1	0	5Y 6/4
2491	84,8	0,3	0,18	tr	1,0	0,00	84,7	6,4	8,9	0	5Y 7/4
2392	80,8	2,4	0,40	2	0,9	0,00	86,2	5,3	8,5	0	5Y 7/4
2493	78,4	2,2	0,59	3	1,3	0,00	81,1	8,1	10,8	3	5Y 7/4
2494	78,2	1,1	0,49	2	1,9	0,00	76,6	11,1	12,2	2	5Y 6/4

SAMPLE NO.	$CaCO_3$	P_2O_5	K_2O	GLAUCO-NITE	ORGANIC CARBON	GRAVEL	SAND	SILT	CLAY	FAECAL PELLETS	COLOUR
CRUISE 244 contd.											
2495	69,1	0,7	0,77	2	2,4	0,00	67,9	14,7	17,3	3	5Y 6/4
2496	2,2	1,4	3,00	28	0,8	0,00	90,1	2,1	7,8	5	5GY 4/2
CRUISE 257											
2676	83,8	0,2	0,46	tr	1,0	0,00	19,4	20,5	59,7	0	5YR 8/1
2677	82,1	0,5	0,51	0	0,7	0,00	32,4	24,6	43,0	0	5YR 8/1
2678	35,7	0,7	1,40	8	2,9	0,00	64,8	17,5	17,7	15	5Y 5/2
2679	11,9	0,4	1,38	tr	1,7	0,98	68,6	19,8	10,6	9	N 7,5
2680	8,3	0,9	1,76	13	2,6	1,22	42,7	28,7	27,4	1	N 7,5
2682	17,4	0,2	1,86	tr	1,1	0,00	80,5	3,8	15,7	4	5Y 5/2
2683	10,2	1,0	3,51	34	3,9	0,00	67,7	15,8	16,5	3	5Y 5/2
2684	16,0	0,5	1,21	tr	1,8	0,00	72,4	14,8	12,7	1	N 7,5
2685	48,2	0,7	1,12	tr	3,4	0,00	59,0	21,0	20,0	25	5Y 6/2
2686	65,9	0,4	0,87	tr	3,2	0,00	57,1	15,1	27,8	11	5Y 5/4
2687	74,3	1,3	0,74	2	2,1	0,00	70,5	13,3	16,1	4	5Y 7/4
2688	67,5	2,6	0,97	10	1,9	0,00	73,5	14,9	11,6	4	5Y 5/4
2689	75,4	2,4	0,89	7	1,6	0,00	74,7	13,1	12,2	5	5Y 7/4
2690	71,1	2,1	0,82	6	1,7	0,00	77,1	11,7	11,3	0	5Y 7/4
2691	74,6	2,1	0,86	8	2,1	0,00	72,6	13,9	13,5	2	5Y 5/2
2692	78,2	0,5	0,53	tr	3,0	0,00	53,4	28,9	17,7	2	5Y 7/4
2693	78,3	4,9	0,31	tr	1,2	0,00	79,0	11,9	9,1	0	5Y 7/4
2694	86,4	0,6	0,23	0	1,7	0,00	65,0	18,8	16,1	0	5Y 7/2
2695	89,9	0,4	0,30	tr	1,3	0,00	65,0	19,2	15,8	0	5Y 7/2
2696	88,0	0,2	0,40	0	1,5	0,00	61,6	22,3	16,1	0	5Y 7/2
2697	86,1	0,2	0,46	0	1,4	0,00	57,2	27,2	15,6	0	5Y 8/2
2698	87,7	0,2	0,30	0	1,4	0,13	62,8	20,2	16,9	0	5Y 7/2
2699	87,5	0,2	0,39	0	1,5	0,00	54,5	25,9	19,6	0	5Y 7/2
2700	83,6	0,9	0,41	tr	1,2	0,76	54,9	23,5	20,8	0	5Y 7/2
2701	86,2	0,9	0,23	0	1,9	0,00	71,1	15,0	13,8	3	5Y 7/4
2702	74,9	5,9	0,30	tr	1,2	0,02	82,7	8,8	8,5	0	5Y 7/4
2703	85,3	1,6	0,30	tr	1,3	0,30	87,0	2,6	10,1	4	5Y 6/4
2704	73,8	3,3	0,76	4	1,6	0,00	75,2	13,8	11,1	5	5Y 5/4
2705	69,8	2,6	0,90	9	1,8	0,00	78,8	10,6	10,7	8	5Y 6/4
2706	65,8	3,4	0,93	7	2,0	0,06	72,6	8,8	18,6	20	5Y 6/4
2707	73,6	2,6	0,70	5	2,0	0,32	74,7	11,3	13,6	3	5Y 5/4
2708	74,6	0,8	0,56	tr	2,4	0,00	73,5	12,5	14,1	4	5Y 5/4
2709	60,5	1,0	0,88	tr	3,4	0,00	64,5	14,1	21,4	21	5Y 5/4

SAMPLE NO.	$CaCO_3$	P_2O_5	K_2O	GLAUCO-NITE	ORGANIC CARBON	GRAVEL	SAND	SILT	CLAY	FAECAL PELLETS	COLOUR
CRUISE 257 contd.											
2710	9,5	0,7	4,67	45	1,8	0,57	75,8	11,0	12,6	8	5GY 4/2
2711	4,7	0,2	1,01	5	1,8	1,06	67,7	13,5	17,5	7	5Y 5/2
2712	5,4	0,8	2,50	0	4,0	0,00	05,8	32,9	61,3	6	5Y 5/2
2713	3,9	0,7	2,02	0	2,3	0,00	45,4	14,8	39,9	2	5Y 5/2
2714	11,5	1,5	2,42	16	1,8	4,70	63,7	15,7	15,9	5	5Y 5/2
2715	39,2	1,4	1,24	2	1,6	0,90	69,3	13,7	16,0	6	5Y 5/2
2716	65,6	0,7	0,94	2	2,7	0,00	63,5	17,8	18,7	8	5Y 6/2
2717	70,4	0,5	2,48	tr	2,8	0,04	60,6	11,4	21,6	13	5Y 6/4
2718	64,8	3,6	1,16	10	1,7	0,00	73,5	11,9	15,1	0	5Y 5/4
2719	71,2	2,1	0,95	10	1,8	0,00	74,7	16,7	13,5	7	5Y 5/4
2720	70,9	2,5	1,10	6	2,5	0,00	64,1	17,2	19,2	6	5Y 5/4
2721	78,5	1,5	0,55	2	1,1	0,00	65,4	9,8	17,4	4	5Y 5/4
2722	80,2	1,8	0,46	2	1,6	0,00	74,6	29,2	15,6	3	5Y 5/4
2723	87,7	0,8	0,32	tr	1,9	0,00	53,6	24,7	17,2	0	5Y 7/4
2724	86,5	0,6	0,28	0	1,7	0,00	52,3	19,6	23,0	0	5Y 7/2
2725	85,5	0,3	0,43	tr	1,5	0,00	56,7	19,6	23,7	0	5Y 7/2
2726A*	85,8	0,3	0,31	tr	2,1	0,00	48,6	23,0	28,4	0	5Y 7/2
2727	86,3	0,2	0,38	tr	1,6	0,00	57,1	20,2	22,8	0	5Y 7/2
2728	88,8	1,4	1,10	tr	1,9	0,00	51,0	20,8	28,2	0	5Y 7/2
2758	33,3	0,3	0,90	tr	1,2	0,27	82,2	6,8	10,8	3	5Y 5/2
2759	22,2	0,4	0,92	tr	1,5	0,00	88,2	7,3	4,5	17	N 7,5
2760	19,5	0,5	1,27	3	2,2	0,00	79,7	12,3	8,0	8	5Y 5/2
CRUISE 259											
2762	2,8	0,7	4,52	47	1,8	0,00	73,2	9,7	17,1	3	10Y 6/2
2763	3,5	0,7	4,42	39	1,1	0,00	76,5	5,9	17,6	3	10Y 6/2
2764	6,1	0,3	0,72	15	0,5	0,00	82,5	4,9	12,6	4	5GY 5/2
2765	4,0	1,4	3,02	34	0,9	0,00	76,4	4,0	19,7	0	5GY 4/2
2766	3,9	2,3	6,59	67	1,5	0,00	81,9	2,8	15,3	0	5GY 4/2
2767	3,1	2,6	6,24	63	0,5	1,12	85,0	3,1	10,8	0	5GY 5/2
2768	20,0	2,0	4,10	45	0,7	0,00	81,0	5,9	13,1	0	5GY 5/2
2769	15,9	3,5	3,20	45	0,6	6,93	77,6	4,7	10,7	0	5GY 4/2
2770	53,9	1,4	2,11	14	1,5	0,00	66,7	13,3	20,0	0	5GY 5/2
2771	42,8	3,1	2,50	16	0,8	0,00	54,3	17,5	28,2	5	5GY 6/2
2772	58,6	2,8	1,40	12	0,3	1,08	58,3	21,7	18,9	0	5GY 5/2
2773	27,0	4,3	5,60	60	0,5	0,01	83,9	4,5	11,6	0	5GY 7/2

* Top of Core

SAMPLE NO.	$CaCO_3$	P_2O_5	K_2O	GLAUCO-NITE	ORGANIC CARBON	GRAVEL	SAND	SILT	CLAY	FAECAL PELLETS	COLOUR
CRUISE 259 contd.											
2774	44,0	2,3	3,30	39	1,3	0,00	70,5	11,5	18,0	0	10Y 6/2
2775	46,4	1,0	2,06	4	1,5	0,00	35,6	29,1	35,3	0	5Y 7/2
2776	57,9	1,4	2,30	14	1,2	0,00	40,9	14,0	45,1	3	5Y 8/2
2777	56,5	2,5	2.60	48	0,9	0,00	72,0	11,6	16,4	0	5Y 7/4
2778B*	39,1	2,2	3,40	41	1,3	0,00	71,1	15,4	13,5	4	5Y 6/4
2779	38,1	2,2	4,13	47	1,6	0,00	74,0	11,5	14,5	3	10Y 6/2
2780	52,2	1,7	2,71	26	1,5	0,00	72,8	12,1	15,3	0	5Y 7/2
2781	50,4	2,0	2,79	29	1,7	0,00	71,7	11,8	14,3	3	10GY 5/2
2782	36,8	3,1	4,27	46	1,1	0,00	82,7	6,8	10,5	0	10Y 6/2
2783	42,3	2,7	3,72	48	1,0	0,00	84,5	5,2	10,3	0	10Y 6/2
2784	45,2	1,6	2,77	21	1,8	0,00	72,8	11,6	15,6	0	5GY 4/2
2785	10,9	2,0	2,60	48	1,0	0,00	85,3	6,3	8,4	0	5GY 4/2
2786	8,6	1,9	2,48	tr	1,0	0,00	40,5	32,5	26,9	14	5GY 4/2
2787	4,1	1,1	3,90	44	0,8	0,00	87,0	3,8	9,2	0	5GY 4/2
2788	4,4	1,0	1,80	12	1,0	0,89	87,1	4,7	7,3	4	10Y 5/2
2789	13,2	1,0	2,70	23	0,9	2,35	68,8	11,2	17,6	8	10Y 5/2
2790	16,9	1,2	2,21	16	1,5	0,00	75,5	11,3	14,4	10	5Y 5/2
2791	19,0	1,0	1,59	8	1,8	0,50	75,6	9,7	14,2	5	5Y 5/2
2792	7,9	1,0	2,45	21	1,1	0,00	86,3	5,9	7,8	4	10Y 6/2
2793	3,5	0,8	1,31	9	1,1	0,00	87,9	4,1	8,0	6	5GY 4/2
2794	4,6	1,1	1,92	14	0,9	0,00	90,5	2,6	7,0	4	10Y 6/2
2795	4,6	1,1	3,11	28	0,7	0,00	86,1	4,4	9,4	3	5GY 4/2
2796	8,2	1,1	4,59	48	0,8	0,00	86,5	5,0	8,5	3	10GY 5/2
2797	5,7	1,2	5,67	65	0,8	0,46	87,0	4,5	8,1	2	10GY 5/2
2798	5,3	1,7	5,81	68	0,6	0,43	86,8	6,3	6,5	3	10GY 5/2
2799	20,0	0,3	2,68	3	0,4	0,39	17,4	57,4	24,9	0	10Y 6/2
2800	4,7	5,4	2,50	9	1,1	13,85	30,7	20,9	34,6	0	10Y 6/2
2801	38,2	0,9	1,90	15	0,8	0,00	80,8	9,0	10,2	3	5Y 8/1
2802	8,8	0,3	1,90	4	0,9	3,35	31,5	49,3	15,9	0	5Y 8/1
2803	39,5	1,0	4,20	38	1,0	0,00	75,1	12,2	12,7	0	N 7,5
2804	53,5	0,7	2,29	26	1,1	0,00	76,7	20,1	11,1	0	N 7,5
2805	87,0	0,3	0,93	tr	1,3	0,00	63,4	3,3	16,5	0	5Y 7/2
2806	1,0	0,9	4,21	72	0,6	0,00	89,1	3,3	7,6	5	10GY 5/2
2807	8,5	1,3	2,94	28	0,8	0,00	88,1	4,4	7,5	4	10Y 5/2
2808	4,4	1,0	1,50	7	0,9	0,00	90,8	3,3	5,9	4	5GY 4/2

* Top of Core

SAMPLE NO.	$CaCO_3$	P_2O_5	K_2O	GLAUCO-NITE	ORGANIC CARBON	GRAVEL	SAND	SILT	CLAY	FAECAL PELLETS	COLOUR
CRUISE 259 contd.											
2809	6,4	1,2	1,96	15	0,9	0,00	86,4	4,6	9,0	4	10Y 6/2
2810	9,7	1,3	1,80	15	1,1	0,00	90,0	4,3	5,7	10	5GY 4/2
2811	10,3	1,5	1,69	14	1,0	0,00	86,9	5,5	7,6	4	10Y 6/2
2812	9,9	2,5	2,23	21	0,8	0,16	88,8	3,3	7,7	0	10Y 5/2
2813	9,0	4,0	3,77	34	0,4	0,34	89,9	3,6	6,2	0	5GY 5/2
2814	13,5	2,3	2,96	28	1,5	0,00	82,5	9,3	8,2	0	10Y 5/2
2815	6,6	0,7	1,26	5	0,9	1,52	90,4	3,3	4,8	0	10Y 6/2
2816	10,7	1,1	1,99	13	1,1	1,02	88,9	4,1	6,0	0	10Y 6/2
2818	31,6	0,5	1,64	8	1,0	0,00	77,1	9,9	13,1	3	10Y 6/2
2819	50,9	0,3	1,15	2	1,5	0,00	49,2	23,9	26,9	1	10Y 6/2
2820	50,1	0,3	1,22	tr	2,0	0,00	42,0	32,2	25,8	1	5Y 6/4
2821	49,4	0,2	1,15	tr	2,6	0,00	27,8	34,6	37,6	2	5Y 7/2
2822B*	24,7	0,2	2,46	13	1,4	11,56	48,6	8,3	31,5	5	5Y 8/2
2823B*	10,4	4,3	3,20	28	0,7	4,00	66,9	7,1	24,0	6	N 7,5
2824	9,8	0,9	1,41	6	1,0	0,30	82,2	7,4	9,9	3	5Y 7/2
2825	18,7	1,6	2,14	14	1,1	0,00	82,4	8,9	8,6	5	10Y 6/2
2826	17,2	0,5	1,29	tr	2,0	0,00	68,6	17,5	13,9	10	5Y 5/2
2827	41,6	0,5	1,60	tr	3,3	0,00	26,6	40,9	32,5	3	5Y 7/2
2828	41,2	0,3	1,32	tr	3,5	0,00	24,3	38,8	36,9	4	5Y 6/2
2829A*	41,3	0,3	1,25	tr	2,0	0,00	43,0	29,7	27,4	0	5Y 6/2
2830	63,8	0,2	1,02	tr	0,7	0,03	29,6	27,7	42,6	0	5Y 8/2
2831	49,6	0,3	1,36	tr	2,5	0,00	15,0	35,4	49,5	0	5Y 7/2
2832	43,1	0,4	1,36	tr	2,7	0,00	18,5	42,2	39,3	0	5Y 7/2
2833	34,2	0,3	1,30	tr	2,0	0,00	47,5	30,1	22,4	2	5Y 7/2
2834	34,0	1,1	2,53	5	1,3	0,00	70,6	15,8	13,5	3	5Y 6/2
2835	15,4	0,7	1,42	3	1,0	0,00	59,3	20,4	20,3	0	5Y 6/2
2836	18,3	1,5	1,34	14	0,8	0,14	79,7	11,2	9,0	0	5Y 7/2
2837	28,6	0,4	1,25	tr	1,7	0,00	53,2	25,9	20,9	2	5Y 7/2
2838	45,8	0,3	1,44	0	1,9	0,00	25,2	37,4	37,3	1	5YR 8/1
CRUISE 261											
2840	16,5	0,4	0,08	0	0,8	0,00	91,3	0,5	8,2	0	5Y 7/2
2843	92,7	0,7	0,15	0	0,8	0,00	96,0	1,2	2,9	0	5Y 8/2
CRUISE 268											
3075	40,4	0,3	0,27	0	0,2	0,60	94,0	2,3	3,1	0	5Y 8/1
3077	22,0	0,4	1,40	tr	1,7	0,00	74,2	15,1	10,8	9	N 7,5

SAMPLE NO.	$CaCO_3$	P_2O_5	K_2O	GLAUCO-NITE	ORGANIC CARBON	GRAVEL	SAND	SILT	CLAY	FAECAL PELLETS	COLOUR
CRUISE 268 contd.											
3079	3,5	0,5	1,60	tr	1,5	0,00	71,4	8,0	20,6	6	5Y 5/2
3082	2,9	0,3	1,20	0	2,0	12,47	25,1	20,0	42,4	0	N 7,5
3085	2,6	0,2	0,67	0	1,6	0,00	84,4	1,7	13,9	12	N 7,5
3086	5,9	0,3	1,80	0	5,2	0,76	78,5	9,2	11,5	42	5Y 5/2
3087	12,9	0,3	1,40	0	4,1	0,00	73,7	7,6	18,8	38	5Y 5/2
3089	56,6	0,2	0,50	0	1,0	44,11	47,3	1,8	6,8	0	5YR 8/1
3090	17,7	0,2	0,91	0	1,4	3,39	82,9	7,2	6,5	9	5Y 7/2
3091	3,5	0,3	1,20	0	0,9	3,30	79,5	4,8	12,4	7	5Y 6/2
3093	2,1	0,3	1,20	0	1,9	1,96	88,0	2,6	7,4	14	5Y 5/2
3094	17,9	0,1	0,32	0	0,3	16,15	71,7	1,5	10,7	0	N 8
3095	12,2	0,2	0,39	tr	0,2	0,00	93,5	4,3	2,2	0	N 8
3097	1,9	0,2	0,43	0	0,7	0,00	88,0	1,4	10,6	0	5Y 8/2
3098	1,3	0,3	0,72	tr	0,6	0,00	81,8	3,1	15,1	0	5Y 6/2
3099	4,4	0,3	2,80	0	5,2	0,40	41,0	24,4	34,2	40	5Y 5/2
3100	4,8	0,60	1,30	tr	1,2	0,00	75,5	11,2	13,3	11	5Y 4/4
3101	20,1	0,4	1,30	tr	1,8	0,00	65,5	17,5	17,1	8	5Y 5/2
3102	16,9	0,4	1,20	tr	1,7	0,00	63,2	24,9	11,9	11	5Y 5/2
3103	20,3	0,6	1,10	tr	1,1	0,27	66,9	20,3	12,5	5	5Y 7/2
3104	29,1	0,6	1,20	3	0,9	0,12	68,2	21,1	10,3	3	5Y 7/2
3105	41,7	2,0	2,00	13	0,8	0,00	67,3	20,3	11,9	0	5Y 7/4
3107	74,5	0,2	0,44	tr	1,4	0,00	52,8	22,9	24,3	0	5Y 8/2
3108	80,4	0,2	0,69	tr	1,0	0,00	36,9	26,8	36,3	0	5Y 8/2
3109	83,6	0,2	0,38	tr	0,7	0,00	50,9	26,7	22,4	0	5Y 8/2
3110	85,1	0,2	0,36	tr	1,6	0,00	56,7	22,1	21,2	0	5Y 7/2
3111	82,8	0,3	0,63	tr	1,5	0,00	53,8	24,9	21,3	0	5Y 7/2
3112	86,6	0,6	0,29	tr	1,6	0,07	53,4	23,8	22,7	0	5Y 7/2
3113	73,1	0,2	0,33	0	1,9	0,00	50,8	29,2	20,0	0	5Y 7/2
3114	83,7	0,2	0,38	0	1,3	0,00	43,0	31,0	26,0	2	5Y 8/2
3115	80,0	0,2	0,51	0	0,9	0,00	22,8	33,0	44,2	1	5Y 8/2
3117	79,5	0,2	0,65	0	1,6	0,00	19,6	36,0	44,4	0	5Y 8/2
3118	47,4	0,3	0,15	tr	0,5	0,00	21,6	41,4	37,0	0	5Y 7/2
3297	4,5	0,2	1,71	0	1,0	0,00	72,8	8,2	18,9	28	N 7,5
3298	6,6	0,3	2,40	0	3,4	0,00	36,9	23,7	39,3	30	5Y 5/2
3299	6,0	0,3	2,40	0	3,5	0,00	30,1	28,8	41,1	30	5Y 5/2
3300	5,9	0,3	2,30	0	4,2	0,00	23,7	27,4	49,0	24	5Y 5/2

SAMPLE NO.	$CaCO_3$	P_2O_5	K_2O	GLAUCO-NITE	ORGANIC CARBON	GRAVEL	SAND	SILT	CLAY	FAECAL PELLETS	COLOUR
CRUISE 268 contd.											
3301	6,1	0,3	2,20	0	3,4	0,17	21,3	31,3	47,2	13	5Y 5/2
3302	5,8	0,3	2,20	0	3,6	0,00	39,7	25,6	34,7	36	5Y 5/2
3304	2,4	0,5	1,10	0	1,5	0,00	70,5	11,1	18,4	7	5Y 5/2
3305	3,9	0,5	1,50	tr	2,0	0,00	61,3	15,9	22,8	13	5Y 5/2
3306	6,9	0,5	2,20	tr	3,5	0,00	49,3	22,7	28,0	31	5Y 5/2
3307	6,9	0,3	2,30	tr	4,2	0,00	42,6	27,6	29,8	42	5Y 5/2
3308	28,1	1,1	1,50	tr	3,4	0,00	48,2	21,0	30,8	10	5Y 6/2
3309	6,4	0,3	2,20	tr	4,6	0,00	37,3	27,0	35,6	37	5Y 6/2
3310	7,1	0,3	2,20	0	5,1	0,00	34,9	25,3	39,8	35	5Y 6/2
3311	9,3	0,5	2,10	0	4,7	0,00	31,9	30,6	37,5	32	5Y 6/2
3312	5,2	0,2	0,93	tr	1,6	0,60	75,1	8,1	16,2	5	N 7,5
3314	8,2	0,4	2,30	0	2,0	0,00	41,5	20,9	37,5	40	5Y 4/4
3315	9,0	0,3	2,30	0	5,6	0,00	50,1	18,1	31,8	49	5Y 4/4
3316	9,1	0,3	2,30	0	4,6	0,00	34,0	24,5	41,5	34	N 7,5
3317	8,0	0,3	1,60	0	2,9	0,00	61,1	13,2	25,7	24	5Y 5/2
3318	7,9	0,1	0,58	0	0,2	0,13	92,1	1,0	6,8	0	5Y 8/1
3319	8,4	0,2	0,63	0	0,2	0,00	83,4	2,4	14,2	0	5Y 8/1
3320	2,9	0,2	3,30	0	0,9	0,74	02,2	46,1	51,0	1	10YR 7/4
3321	3,6	0,2	3,40	0	1,6	0,00	03,7	30,8	65,5	2	10YR 7/2
3322	7,6	0,2	2,90	0	4,8	0,00	20,7	25,5	53,8	21	N 7,5
3323	6,9	0,4	2,60	0	5,4	0,00	41,3	16,7	42,0	41	5Y 5/2
3324	45,8	0,1	0,3	0	0,7	71,86	25,7	0,7	1,8	0	5Y 8/2
3327	4,6	0,5	2,60	0	1,5	0,30	43,4	22,0	34,3	42	5Y 5/2
CRUISE 273											
3337	66,8	0,2	0,77	0	1,0	0,00	56,4	23,1	20,5	0	5Y 8/2
3338	70,4	0,3	0,74	0	1,1	0,00	60,8	28,9	10,3	0	5Y 7/2
3339	68,8	0,2	0,84	0	1,1	0,00	28,8	30,7	40,5	1	5Y 8/2
3340	69,2	0,3	0,77	tr	0,9	0,00	51,1	24,7	24,2	0	5Y 8/2
3341	57,2	0,9	1,70	14	1,1	0,00	65,2	19,6	15,2	0	10Y 7/2
3342	73,4	0,2	0,73	0	1,3	0,00	19,8	31,7	48,5	0	5Y 8/2
3343	80,1	0,2	0,48	0	0,8	0,00	26,7	28,7	44,6	0	5Y 8/2
3344	80,5	0,3	0,75	0	1,0	0,00	30,4	27,1	42,5	0	5Y 8/2
3345	85,4	0,2	0,35	0	1,1	0,00	58,4	24,0	17,6	0	5Y 8/2
3346	85,1	0,2	0,28	0	1,6	0,00	59,2	25,6	15,3	0	5Y 7/2
3347	79,5	0,5	0,54	0	1,2	0,00	14,8	28,3	56,9	0	5Y 8/2

SAMPLE NO.	$CaCO_3$	P_2O_5	K_2O	GLAUCO-NITE	ORGANIC CARBON	GRAVEL	SAND	SILT	CLAY	FAECAL PELLETS	COLOUR
CRUISE 273 contd.											
3348	83,3	0,2	0,53	0	0,7	0,00	48,9	24,3	26,8	0	5Y 8/2
3349	79,1	0,1	0,94	0	0,7	0,00	31,3	19,1	49,7	0	5Y 8/2
3350	94,7	0,2	0,53	0	0,9	0,00	24,3	33,3	42,4	0	5Y 8/2
3573	72,2	2,6	0,79	3	1,7	0,00	74,1	14,4	11,6	4	5Y 5/4
3574	67,2	5,3	1,40	15	1,8	0,00	77,0	8,4	14,6	6	5Y 5/4
3575	69,0	3,1	0,91	4	1,7	0,00	74,3	9,8	15,9	8	5Y 5/4
3576	75,3	2,5	0,94	4	1,6	0,00	71,7	16,1	12,9	0	5Y 6/4
3577	83,9	0,5	0,37	tr	1,6	0,00	57,3	19,1	23,4	0	5Y 7/2
3578	71,4	0,9	1,40	11	1,7	0,02	59,7	11,4	28,9	0	5Y 6/4
3579	53,0	1,6	2,60	20	1,2	0,00	68,8	16,9	14,3	0	N 7,5
3580	46,8	2,1	1,50	11	0,7	0,00	85,5	10,7	3,8	0	N 7,5
3581	27,3	0,7	1,20	0	0,9	1,10	75,9	15,3	7,7	0	5Y 6/2
3582	21,1	0,4	1,20	tr	2,0	0,03	61,5	27,3	10,9	8	N 7,5
3584	7,7	2,6	3,40	25	2,7	0,00	78,6	15,7	7,7	28	5GY 4/2
3585	8,5	0,9	3,00	24	2,6	0,07	79,2	12,1	8,6	20	5Y 5/2
3586	17,3	0,4	1,55	2	3,7	0,00	76,0	16,4	8,6	42	5Y 5/2
3587	33,5	0,4	1,08	tr	2,8	0,26	74,0	14,2	11,5	11	N 7,5
3590	28,0	0,4	0,57	2	0,6	0,00	93,9	3,2	2,8	0	10Y 7/2
3591	21,5	0,4	0,58	0	0,4	0,02	93,8	3,9	2,3	3	5Y 7/2
3592	41,0	0,1	0,54	0	0,1	8,74	84,3	1,3	4,8	0	5Y 7/2
3593	44,7	0,1	0,82	0	0,3	15,00	85,0	0,0	0,0	0	5YR 8/1
CRUISE 300											
4634	4,0	0,4	1,60	0	3,2	0,00	11,1	24,6	64,3	5	5Y 5/2
4635	3,2	0,4	2,30	2	2,6	22,50	26,0	24,1	27,6	23	5Y 5/2

APPENDIX III - GEOCHEMICAL AND MINERALOGICAL INVESTIGATIONS OF THE <2μm FRACTION: METHODS AND RESULTS

III - A. Mineralogical techniques

(i) Sample recovery.
(ii) Sedimentation.
(iii) Pre-treatment.
(iv) Mounting
(v) X-ray diffraction procedure and mineral identification.
(vi) Semi-quantitative analyses.

III - B. Geochemical techniques

(i) Sample collection and storage.
(ii) Dialysis.
(iii) The concentration of <2μm material for geochemical analysis.
(iv) Dissolution and analytical procedures.
(v) Element partitioning.
(vi) Precision and accuracy.

III - C. Mineralogical results

(i) Semi-quantitative analysis of the <2μm fraction.
(ii) Semi-quantitative analysis of the 2-15μm fraction (on file at University of Cape Town).

III - D. Geochemical results

(i) Geochemical analyses of the <2μm fraction.
(ii) Results of partition study.
(iii) P_2O_5 and K_2O analyses of the <63μm fraction (on file at University of Cape Town).

APPENDIX III - GEOCHEMICAL AND MINERALOGICAL INVESTIGATIONS OF THE <2μm FRACTION: METHODS AND RESULTS

Clay mineral research is complex and as yet studies in this field have not reached the stage where pre-treatment, analytical methods, computation of results etc. have been standardized (Pierce and Seigal, 1969). It is therefore important that the likely sources of error in the methods employed and the precautionary measures that are taken during the study, as well as the precision and accuracy of the determinations are recorded in detail.

III - A. Mineralogical techniques

(i) Sample recovery.

In this study grabs were used in the shoaler regions (<250 m) to recover sediment from the continental margin, and a gravity corer was employed in the deeper parts (see sample map). Recent investigations (Siegal and Pierce, 1973) have shown that the clay mineral contents of samples show significant (at the 95% confidence level) differences according to the type of sampler used. As yet the reason for this discrepancy is not known.

Although no test was made during this study, it is possible that variations in the clay mineral content of the samples could be partly due to differences in the sampling depth between the corer and the grab.

(ii) Sedimentation.

Sedimentation (Jackson, 1956) or centrifuging (Hathaway, 1956) is mainly used to collect clay-size (<2μm) material for clay mineral research. It appears from recent studies (Spoljavic, 1971(a) and (b) and Gibbs, 1971), that equivalent spherical diametre theory is not always applicable in calculating the settling rates of small plate-shaped particles. Moreover, because the geochemical study precluded the use of a dispersing agent (Meade, 1967, p.C66), clay particles have undergone some degree of flocculation while settling. Whether a dispersing agent is used or not, flocculation varies according to the mineral assemblage; the thickness of suspension; the amount of organic material; the type of oxide coating; and the exchange cation content of the samples (Gibbs, 1965, Hathaway, pers.comm. and Pierce, pers.comm.), as well as with temperature (Birch, 1971). During sedimentation some flocculation was observed, especially in river samples, substantiating that irregular settling does occur during the separating process.

It is possible, therefore, that because of an imperfect knowledge of the settling behaviour of clay-size material and due to a lack of control on flocculation from sample to sample, some of the chemical and mineralogical variations determined in this study may be due partly to inaccuracies in the size segregation procedure.

(iii) Pre-treatment.

Calcium carbonate was removed with dilute (4:1) glacial acetic acid and the sample washed three times with distilled water. The acid was not buffered with sodium acetate as this is regarded by clay mineralogists as unnecessary (Hathaway, pers. comm.).

In contrast to the findings of Schoen et al (1972) and Anderson(1963), higher peak to background values were obtained in a pilot study using hydrogen peroxide than when employing sodium hypochlorite. Consequently all samples were pre-treated with 30% hydrogen peroxide to remove organic matter. In the pilot study secondary Fe was removed from the clay samples by ammonium oxalate treatment (Le Riche and Weir, 1963, and Gad and Le Riche, 1966), but as this procedure had no appreciable effect on the X-ray diffractograms, the process was not carried out during subsequent analyses.

As interlayer cations retain different amounts of water of hydration, the clay was also homo-ionically saturated with Mg to ensure that expansion as a result of hydration would be uniform. A 3N magnesium chloride solution was added to an acidified (pH 3,5 to 4,0) clay suspension in a 3:1 ratio so as to render the suspension approximately 1N with respect to Mg. The sample was then shaken gently for 4 hours and washed 3 times to remove excess Mg solution.

(iv) Mounting.

It has been found (Sudo et al, 1961) that sample thickness is of fundamental importance. If the mount is too thin peaks are weak and diffuse and if the slide is too thick a high background is produced (Carrol, 1970). The sample should ideally be between 0, 07 and 0,12 mm thick (Klug and Alexander, 1962), and Sudo et al, 1961).

In this study approximately 0,5 - 0,8 mg of prepared clay material was eye-dropped onto glass slides and quickly dried (less 10 minutes) under an infra-red lamp at a maximum temperature of 50°C.

(v) X-ray diffraction procedure and mineral identification.

In this study two magnesium-saturated clay slides were prepared for each sample. One slide was used for diffracting the untreated clay sample and this was again X-rayed after heating to 550°C for one hour. The other slide was glycolated with ethylene glycol. Initial attempts to glycolate by fuming and by applying the glycol directly onto the edges of the glass-slide and allowing the solution to diffuse through the clay failed. Eventually expansion of the montmorillonitic clays was achieved by carefully painting glycol onto the clay surface on the slide with a very fine brush. Untreated slides were scanned from 3 to 30°2θ at 1°2θ per minute and heated and glycolated samples from 3-13°2θ at the same speed.

A Phillips X-ray diffractometer unit fitted with a Geiger detector employing

Ni-filtered CuKα radiation was used with the following settings: kV=48; mA=20; proportional counter=45; rate meter=4 x 10^2; time constant=1; windows= 1^o/.1mm/1^o; and attenuation=2.

Mineral identification was made by observing the characteristic basal reflection maxima (Fig.AIII-1). Illite was recognised by its 10,5 and 2,3Å peaks which are not affected by heat or glycol treatment. Montmorillonite was detected by its 14Å reflection which expands to 17Å on glycolation and which collapses on heating to 550°C. Special attention was given to the identification of chlorite and kaolinite because of their similar d-spacings of the (002) and (001) reflections at 7Å respectively. Various techniques have been used to distinguish kaolinite from chlorite most of whichinvolve thermal and/or chemical treatment prior to X-raying. Biscaye (1964) has described a method for routinely differentiating kaolinite and chlorite by resolving their 2nd and 4th order basal diffraction peaks at 3,5Å. Chlorite was found to be absent or present in only minor quantities when the samples were run at a slow speed ($\frac{1}{2}^o$/min.) across this dual reflection.

Preferential destruction of kaolinite by heating to approximately 550°C has also been used (Dixon and Jackson, 1960) as a criterion to distinguish these two minerals. However, the behaviour of poorly crystalline materials, such as that found in recent sediments is variable and temperatures as low as 450°C may decompose some chlorites completely, leaving kaolinite little affected (Brown, 1961). Three samples containing illite, montmorillonite, kaolinite and chlorite were heated to 550°C in 100°C intervals to examine the response of these marine clays to thermal treatment. Montmorillonite collapsed at 300°C causing enhancement of the illite reflection and at 500°C the reflection at 7Å was destroyed. At 550°C the low angle background became depressed enough to reveal the presence of a broad chlorite peak at 14Å. The same samples were boiled in 6N hydrochloric acid at 80°C for 18 hours. Kaolinite is not ordinarily decomposed by this treatment (Brown, 1961) and the persistence of a 7Å reflection and the non-appearance of the 14Å peak on heating facilitated the recognition of both kaolinite and chlorite in these samples. Subsequent to this investigation the recognition of chlorite in the presence of kaolinite was made on a routine basis by the occurrence of a reflection at 14Å on a diffractogram of a heated slide.

(vi) Semi-quantitative analyses.

Most semi-quantitative analyses (those not employing interal standards) are based on an early report by Johns et al. (1954). Some of the more important contributions have come from Schultz (1960 and 1964), Griffen and Goldberg (1963) and Meade (1967).

A recent study on the relationship between 5 of the most commonly used semi-quantitative methods has been made by Pierce and Siegal (1969). The large

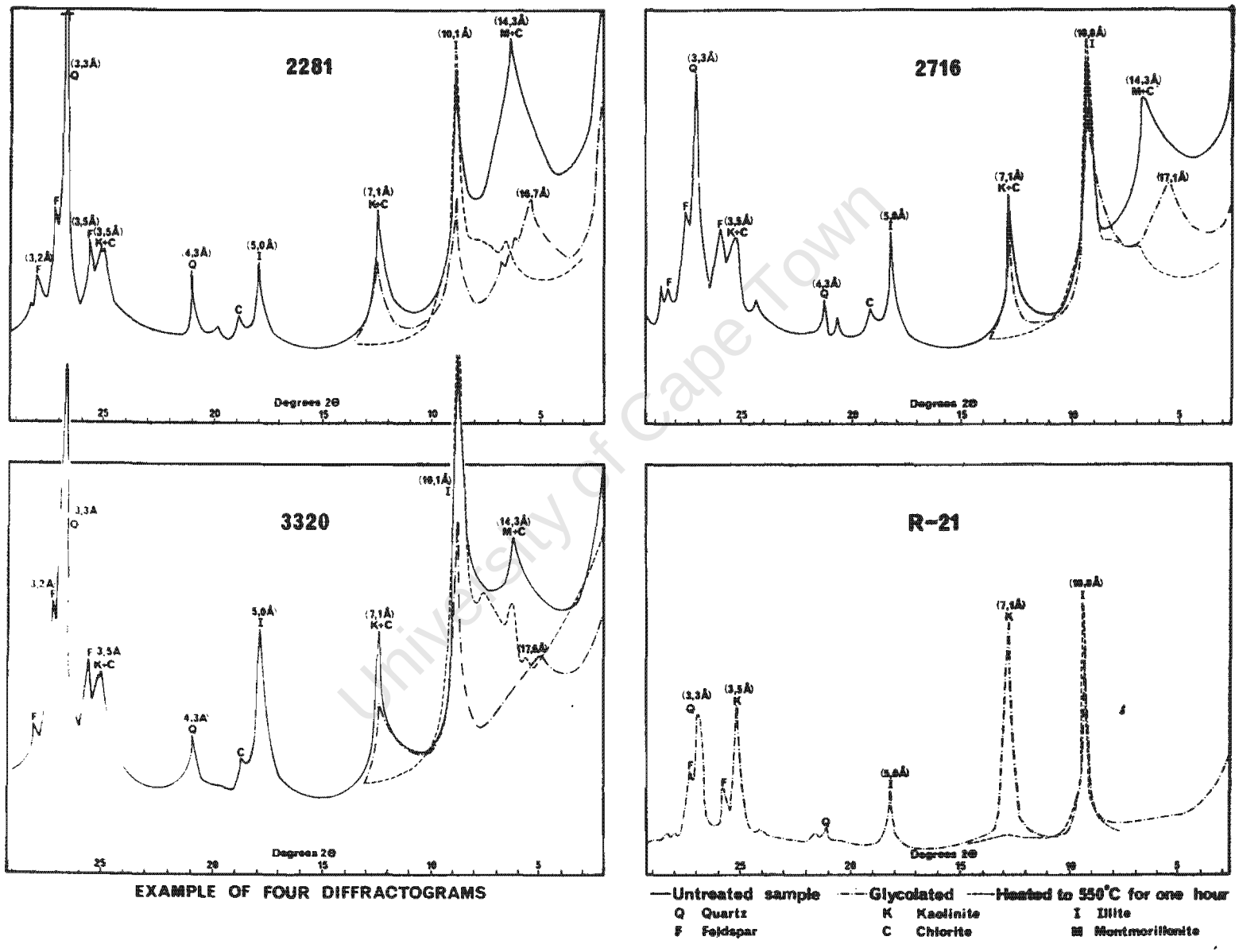


Figure AIII-1

discrepancies in the results of the 5 methods for the same sample have been used by the authors to emphasize the urgent need for standardization in sample preparation, analytical methods and semi-quantitative computations. The present lack of standardization means that inter-area comparisons cannot be accurately assessed.

In this investigation semi-quantitative determinations were made by weighting the integrated peak areas on the glycolated diffractograms (Johns et al., 1954). As poor resolution of the 3,5Å peak occasionally prevented a quantitative estimate of the chlorite/kaolinite content to be made and because only minor chlorite was present in these samples, the area under the 7Å reflection was totally assigned to kaolinite. The chlorite abundance was later estimated by a method described by Schultz (1964). Schultz found that for the Pierre Shale the amount of decrease in the height of the 7Å peak due to the removal of chlorite by acid treatment averages two-thirds of the height of the chlorite peak at 14Å after heating at 550°C and before treating with hydrochloric acid. Therefore the part of the 7Å peak that is attributed to reflections from chlorite is calculated by multiplying the height of the 14Å peak obtained after heating by a factor of two-thirds. The remainder of the 7Å peak height is assigned to kaolinite. Although the thermal characteristics of the Pierre Shale and the clays from the recent sediment off the Cape west coast are undoubtedly different, this method provided a means of estimating the relative abundance of chlorite between samples. However, it was found most convenient to portray the regional distribution of chlorite as a ratio in terms of illite simply on an integrated peak-area basis.

Splits of four clay samples (nos. 2281, 2716, 3320, and R-21) were sent to various geological institutions to assess the variation in a semi-quantitative mineralogical study. Diffractograms and semi-quantitative analyses were returned by Woods Hole Oceanographic Institution (U.S.A.) and Stellenbosch University (South Africa). The results of this investigation are presented in Figures AIII-2 and 3. Bearing in mind the lack of standardization, the results of these determinations are remarkably consistent.

The empirical measure described by Biscaye (1965) was used to measure the crystallinity of the montmorillonite mineral, and an estimation of the K- and plagioclase feldspars distribution was made on a ratio of their peak areas at 3,20 and 3,18Å respectively.

III - B. Geochemical techniques

(i) Sample collection and storage.

The samples used in this study were recovered using metallic grabs and corers, and were stored wet and unfrozen in airtight plastic containers. Before geochemical work could be contemplated it was necessary to establish whether

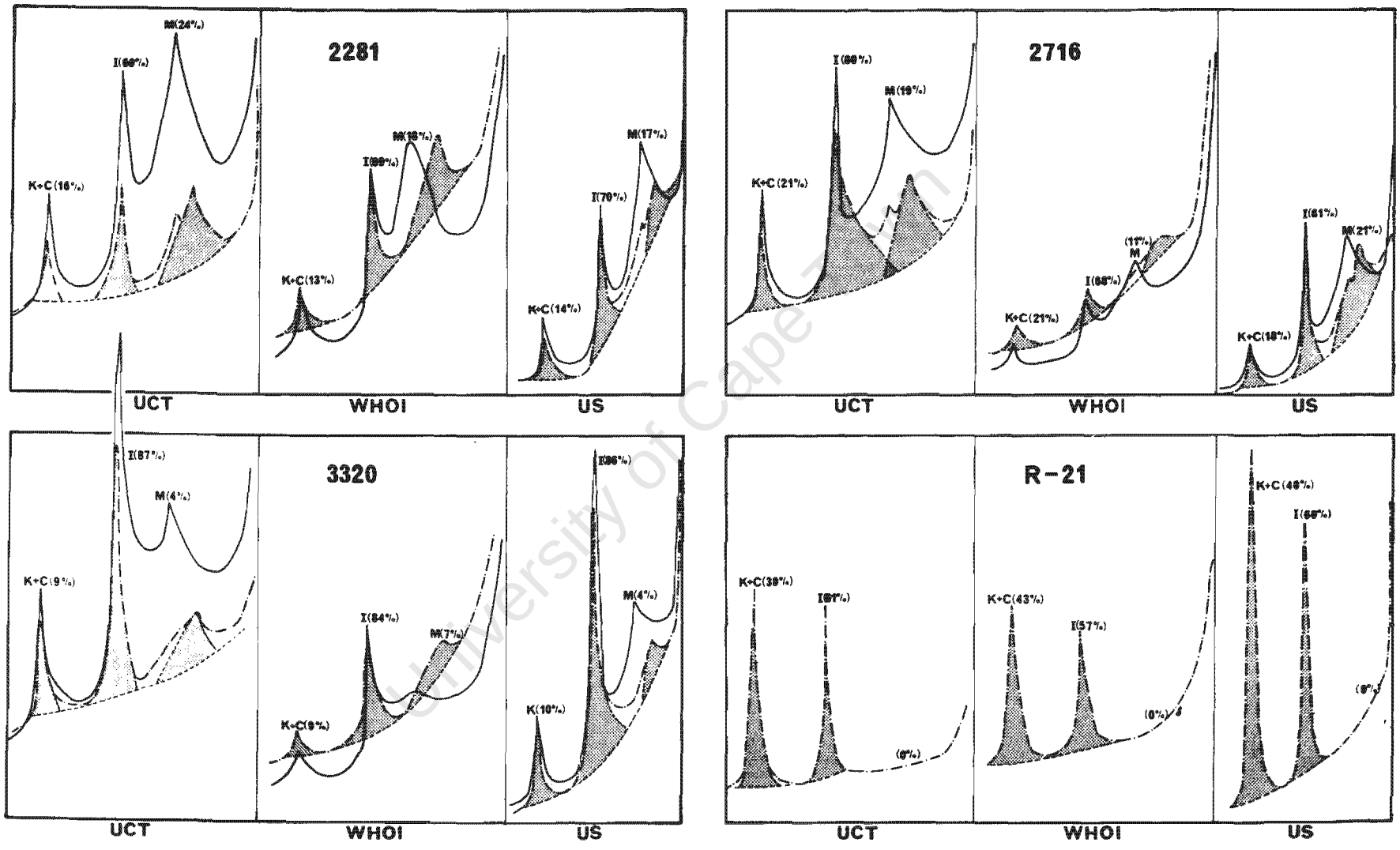


Figure AIII-2

Semi-quantitative analyses of clay mineral abundance made by three geological institutions

SAMPLE	MONTMORILLONITE			ILLITE			KAOLINITE		
	UCT	WHOI	US	UCT	WHOI	US	UCT	WHOI	US
2281	24	18	17	60	69	70	16	13	14
2716	19	11	21	60	68	61	21	21	18
3320	4	7	4	87	84	86	9	9	10
R-21	0	0	0	61	57	60	39	43	40

UCT: University of Cape Town. WHOI: Woods Hole Oceanographic Institution.
US: University of Stellenbosch

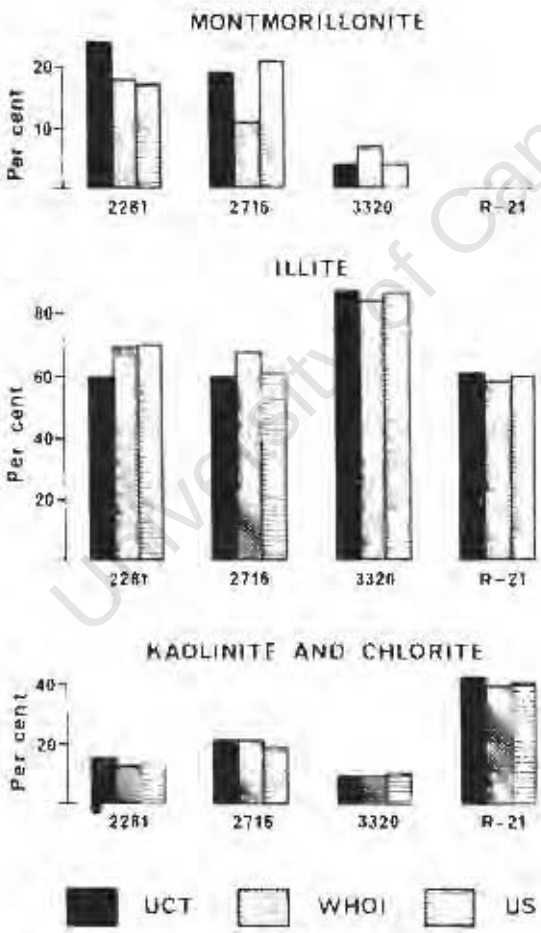


Figure AIII-3

samples were contaminated during retrieval or whether chemical changes, such as sorption on the walls of the container, had taken place during storage. As no equivalent study could be found in the literature it was considered necessary to undertake a special investigation.

A test station was selected on the inner shelf south of Cape Town in an extensive faecal pellet mud belt. This area was chosen because of its homogeneity and because the sediment is muddy and organic-rich, which improves the possibility of it containing abundant trace elements (Calvert and Price, 1970). To preclude metallic contamination from retrieval gear, a non-metallic corer was constructed from PVC tubing. The Pb with which it was weighted was completely sealed within PVC and, as an additional precaution, the corer was attached to 20 metres of plastic-coated wire to minimise contamination by the galvanized hydrowinch cable. One sample was recovered using a galvanized iron grab, weighted externally with Pb, another by means of a short gravity corer made of Cu, Pb and steel, and another using the non-metallic corer. The ship's drift during sampling was approximately one kilometre. Unfortunately it was not possible to take a second sample with the non-metallic corer to determine the variation in geochemistry of the sediment over this distance, but, because of the homogeneous nature of the sediment, it has been considered negligible in this study.

Several subsamples of each sample were taken to investigate: (1) contamination which occurs when sediment is scraped from the metallic surfaces of the grab and core, (2) the effect of pre-treating the inner surfaces of the plastic storage tub with dilute hydrochloric acid to minimise the sorption of elements onto the walls of the container, and (3) whether freezing prevents the loss of elements from sediment during storage.

Six metals (Zn, Mn, Pb, Fe, Cu and Ni) which were considered possible contaminants from the retrieval gear were analyzed approximately two months after recovery by atomic absorption spectroscopy.

Results of the analyses are presented in Table AIII-1. The Mann-Witney U test (Siegel, 1956) was used to test for significant differences between the various groups of subsamples. This non-parametric test was selected because it does not require the data to be normally distributed, whereas it maintains approximately 80% of the power of the students t-test (Siegel, 1956). Results of the test indicate that significant Zn, Mn and Ni contamination, to the value of approximately 10% of the metal concentration in the sample, occurred in samples retrieved using metallic gear. (An analysis of distilled water run over the surface of the galvanized surface of the grab in the laboratory showed only Zn). No significant differences could be found between the other groups of data, indicating that no significant losses had taken place from samples stored unfrozen in untreated plastic containers.

Table AIII-1. Results of contamination study and precision of the method employed.

ELEMENTS	METALLIC GRAB						METALLIC CORER				NON-METALLIC CORER			
	sediment scraped from walls		sediment from centre of grab				sediment from cutting edge		sediment from inner lining		No acid treatment		acid treated	
			no acid treatment		acid treated									
	unfrozen	frozen	unfrozen	frozen	unfrozen	frozen	unfrozen	frozen	unfrozen	frozen	unfrozen	frozen	unfrozen	frozen
Fe	2,36	2,37	2,39	2,44	2,30	2,36	2,37	2,50	2,35	2,37	2,46	2,42	2,40	2,31
Mn	82	85	87	89	84	86	88	86	85	87	75	74	77	75
Cu	22	23	26	23	22	23	25	27	24	26	26	23	22	25
Ni	50	55	58	58	51	58	51	58	51	50	43	44	45	43
Pb	72	69	64	70	68	70	63	69	66	67	70	71	69	72
Zn	75	75	79	83	75	88	81	81	79	78	63	66	65	65

Precision for the determinations of the above elements at the 95% confidence level.

	iron %	lead ppm	zinc ppm	nickel ppm	manganese ppm	potassium %	copper ppm
A	1,24	19	80	58	86	7,10	23
B	1,36	19	80	58	88	6,99	28
C	1,16	33	73	50	80	6,79	23
D	1,28	18	100	52	86	6,79	28
E	1,32	29	78	58	87	6,79	26
F	1,25	33	75	52	82	6,99	26
G	1,28	29	77	58	84	6,89	26
H	1,32	20	95	50	90	7,20	23
I	1,40	19	75	58	86	7,31	26
J	1,27	30	74	50	84	6,99	23
$\bar{x}$	1,29	24,9	80,7	54,4	85,3	6,98	25,20
Sx	0,07	6,38	9,24	3,86	2,91	0,18	2,04
R.D.	5,43	25,62	11,45	7,10	3,41	2,58	8,09

Fe in per cent, other values in ppm.
$\bar{X}$ - Mean
Sx - Standard deviation
R.D.- Relative deviation

(ii) Dialysis.

Before commencing with geochemical analysis, it was also necessary to determine that elements were not stripped from the clay minerals during dialysis, a process used to remove intestitial salt from marine sediments, and that no contamination from the containers or dialysing tubing occurred.

Two samples were placed in dialysing tubing and immersed in distilled water which was analyzed by atomic absorption regularly, over a period of approximately $1\frac{1}{2}$ days, for Na, Mg, K, Ca and also the elements being studied (Zn, Cu, Fe, Ni, Pb and Mn). Most of the interstitial sea water was removed within the first five to six hours (Fig.AIII-4). After 2000 minutes ($\pm 1\frac{1}{2}$ days) the distilled water was renewed and re-analysed over a further period of 1440 minutes (1 day) to make sure that sorption had not ceased because of a weak ionic gradient.

Negligible amounts of Zn, Cu, Fe were found in the distilled water, and Ni, Pb and Mn were not detected at all, indicating that the dialysis process is not powerful enough to strip adsorbed elements from the sediment. Dialysing tubing (approx. 1 metre in length) soaked in distilled water for 3440 minutes (over 2 days) did not release detectable amounts of any of the elements studied. Blanks run on the distilled water and tap water are also included in Table AIII-2.

(iii) The concentration of <2μm material by sedimentation for geochemical analysis.

To collect sufficient <2μm material for analysis by sedimentation several suspensions needed to be siphoned off. The number of suspensions removed differed from sample to sample and although care was taken to continue the process until a reasonably clear suspension was attained, different amounts of <2μm material undoubtedly remained in the residue (coarse fraction). The flocculation characteristics of samples differed and therefore the proportion of total <2μm material in the sediment which was actually removed is different for each sample.

Analyses were made of the <2μm material recovered during repeated fractionation of sample 3323 to determine whether the composition of the various suspensions changed. The procedure was repeated using the same sample to give an indication of the reproducibility of sedimentation as a geochemical technique (Fig.AIII-5).

Results indicate that,except for the Mn (which varied between 7-16%) content, the trace element composition of the material removed during repeated fraction is consistent. Moreover, the material removed by the 4th and 5th fractionations is small (<10%) so that it has little effect on the composition of the final <2μm samples.

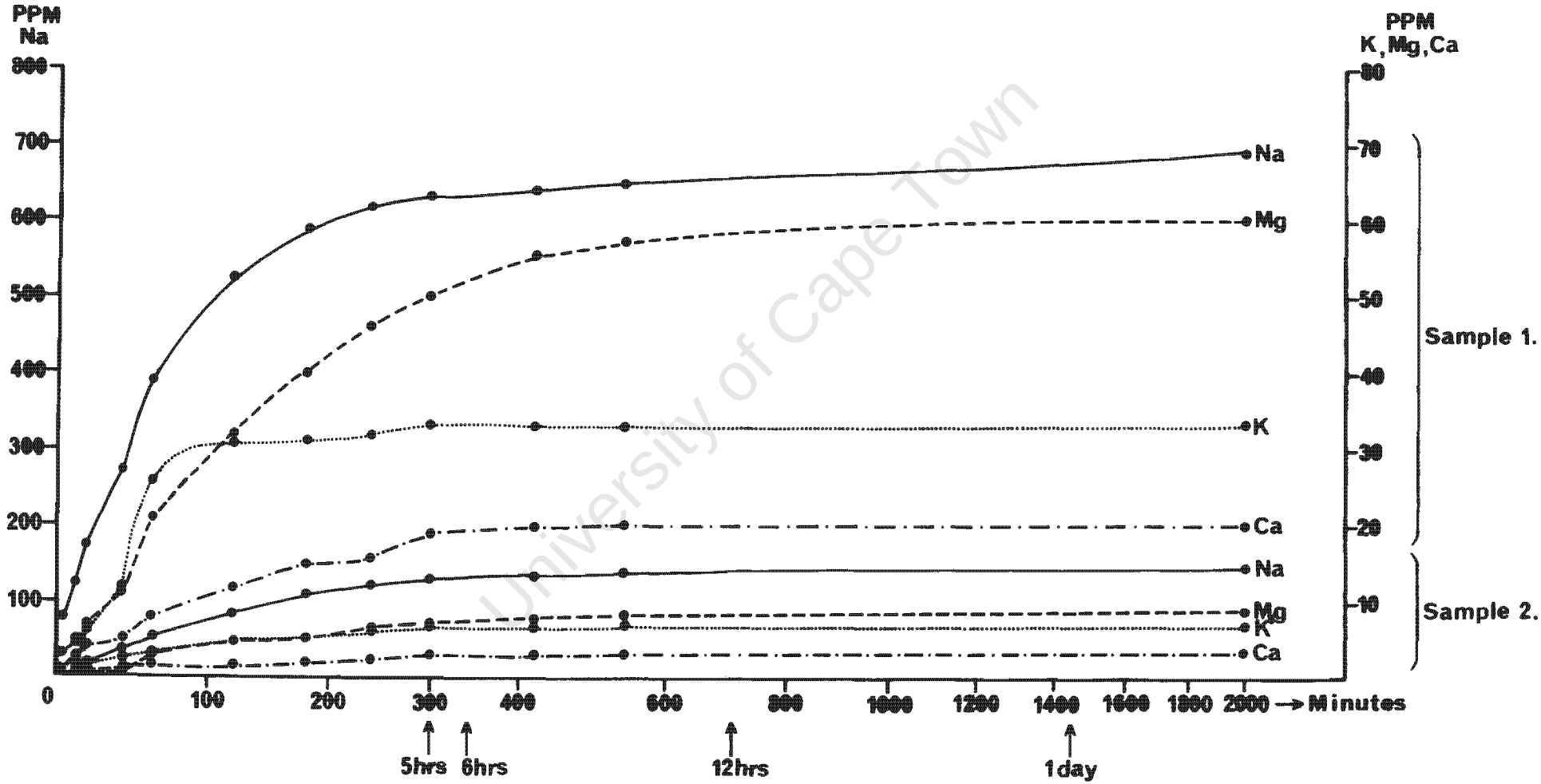


Figure AIII-4

Table AIII-2. The rate at which some elements are removed from marine sediment by dialysis

TIME (Mins)	SAMPLE NO. 1 PPM Na	K	Mg	Ca	Zn	Cu	Fe	SAMPLE NO. 2 PPM Na	K	Mg	Ca	Zn	Cu	Fe
5	n.d.	0,5	0,3	0,5	0,01	0,08	0,04	79	3,7	2,6	1,2	0,02	0,05	n.d.
10	12	0,9	0,5	0,4	0,01	0,08	0,04	127	4,6	4,7	2,1	0,02	0,05	n.d.
15	17	1,2	0,7	0,5	0,02	0,08	0,08	178	6,1	6,1	2,7	0,02	0,05	0,08
30	35	2,1	1,0	0,6	0,02	n.d.	n.d.	270	12	10,8	4,8	0,01	0,04	0,03
60	56	3,3	2,8	1,1	0,02	n.d.	n.d.	395	26	21	8,0	0,01	0,04	0,09
120	85	4,8	4,4	1,8	0,01	0,01	n.d.	524	31	32	12,1	0,01	0,01	0,09
180	111	5,7	5,6	2,2	0,01	0,02	n.d.	595	31	40	15	0,01	0,03	0,09
240	119	6,2	6,5	2,5	0,01	0,01	n.d.	620	32	46	16	0,01	0,02	0,06
300	130	6,6	7,0	2,8	0,01	0,02	n.d.	632	33	50	18	0,01	0,01	0,06
420	134	6,9	7,9	3,1	0,01	n.d.	n.d.	642	33	56	20	n.d.	0,01	0,06
540	144	6,9	8,5	3,4	0,01	n.d.	n.d.	652	33	60	21	0,01	0,01	n.d.
2000	145	7,4	8,8	3,6	0,01	n.d.	n.d.	690	33	67	21	0,01	n.d.	n.d.
	WATER CHANGE							WATER CHANGE						
420	14	1,0	0,9	0,4	n.d.	n.d.		7,8	2,8	7,2	1,5	n.d.	n.d.	n.d.
1440	17	1,6	1,0	0,7	0,01	n.d.		7,8	3,2	8,7	1,9	0,01	n.d.	n.d.
Dializing tubing	0,8	0,14	n.d.	n.d.	n.d.	n.d.								
Tapwater	13	0,7	1,7	15	0,08	0,1								
Distilled water	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.								

n.d. = not detected

Ni, Pb and Mn were not detected

It can be concluded that the first three fractionations remove over 90% of the <2μm material from the sediment and that the variation in the trace element content of these fractionates lies well within the precision of the overall study (see section (vi) Precision and Accuracy).

(iv) Dissolution and analytical procedures.

Exactly 0,5 g of crushed clay was treated with 10 ml of 50% glacial acetic acid (all reagents used were of Analar grade or equivalent) to remove the carbonate and then evaporated to dryness in a platinum dish. The residue was treated with a mixture of 10 ml perchloric and 10 ml hydrofluoric acid and again evaporated to dryness but not baked. Finally, the sample was re-dissolved in 50% HCl, transferred to a volumetric flask and diluted to 50 ml. Blanks were made after approximately each batch of 10 samples.

For the Al and Ca determinations a 2 ml aliquot of the prepared sample was pipetted into 200 ml of distilled water and 5 ml of this solution was added to 5 ml of a 1% potassium chloride solution. This procedure effectively dilutes the sample, and the K suppresses ionization in the nitrous oxide flame thus improving sensitivity.

The samples were anlaysed under Dr. M.J. Orren's supervision on a Varian Techtron Model AA-6 atomic absorption spectrophotometer using the following instrument settings (Varian Techtron, 1973):-

Element	Wavelength nm	slit width(nm)	lamp current(mA)	Flame
Al	309,3	0,5	5	Nitrous oxide-Acetylene
Ca	422,7	0,2	4	Nitrous oxide-Acetylene
Cu	324,8	0,5	3	Air-Acetylene
Fe	246,3	0,2	5	Air-Acetylene
K	404,4	1,0	5	Air-Acetylene
Mn	279,5	0,2	5	Air-Acetylene
Ni	232,0	0,2	5	Air-Acetylene
Pb	217,0	1,0	5	Air-Acetylene
Zn	213,9	0,5	5	Air-Acetylene

(v) Element partitioning.

Many attempts have been made to study element partitioning by subjecting the total sediment to selective chemical attack. Hirst and Nichols (1958) used 25% V/V acetic acid to separate the detrital and non-detrital fractions of carbonate rocks on the understanding that this will not attack the clay mineral lattice (Ray, Gault and Dodd, 1957). The chelating action of E.D.T.A. has also been used (Goldberg and Arrhenius, 1958) to study the trace element distribution in marine sediment. Sulphides have been dissolved and organic

Trace element composition of four fractionates removed during repeated sedimentation.

Sample	wt.% removed by each fractionation	Fe(1)	Mn	Ni	Zn	Pb	K(1)
A1	54	8,70	288	90	196	4	1,62
2	27	8,85	288	96	192	2	1,62
3	13	8,67	273	96	189	1	1,61
(4+5)	(6)+(1)	9,04	269	99	163	11	1,63
TOTAL SEDI-MENT(2)	100	8,85	288	94	194		1,64

Sample	wt.% removed by each fractionation	Fe(1)	Mn	Ni	Zn	Pb	K(1)
B1	50	8,70	288	90	180	3	1,68
2	29	8,40	288	90	196	3	1,62
3	14	8,85	266	76	193	1	1,66
(4+5)	(6)+(2)	8,30	242	63	174	0	1,60
TOTAL SEDI-MENT	100	8,61	282	86	186		1,65

NOTES: (1) values in %, others in ppm.
(2) calculated by considering the trace element concentration of each fractionate and its percentage contribution to the total <2µm sample.

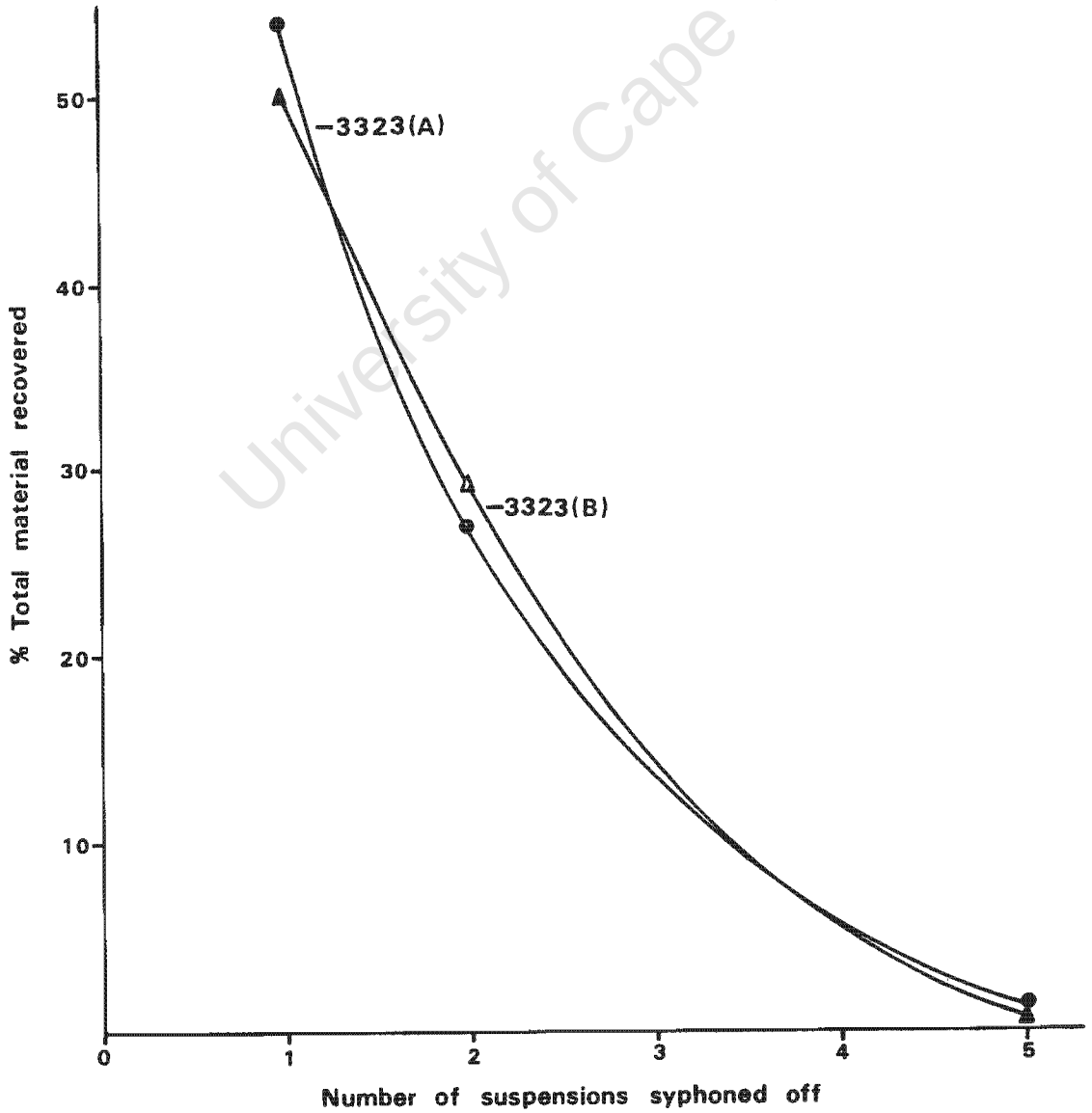


FIGURE AIII-5.

matter partly destroyed by hydrogen peroxide treatment, whereas acid ammonium oxalate in ultra-violet light has been used (Gad et al., 1966) to dissolve some of the iron and aluminium. Chester and Hughes (1967) have combined a reducing agent (1M-hydroxylamine hydrochloride) with 25% acetic acid to produce a more effective separation agent. Recently Marchant (1970) extracted the organic phase from sedimentary rocks by treating crushed rock ultrasonically in a 9:1(V/V) solution of benzene/methanol. This method proved unsuccessful when applied to modern unconsolidated marine sediment from the Cape west coast.

Currently fewer partitioning studies are being reported and researchers in this field (Drs. Curtis, Tourtelot and La Riche, pers.comm.) advise extreme caution when attempts are made to separate the detrital and non-detrital fractions. Some workers (Dr. Hirst, pers.comm.) maintain that a better understanding of the process by which elements are incorporated into the sediment may be attained by using multi-component data computing techniques.

In this study 3 batches of samples from four localities were subjected to glacial acetic acid; acid/reducing and hydrogen peroxide treatments.

In the first batch, approximately 0,5 to 1,0 g of sample (more sample for the calcareous clays) was treated with 50 ml of 25%(V/V) glacial acetic acid (Hirst and Nichols, 1958 and Hirst, 1971). Acid was added until all effervescence ceased, after which the solution was filtered and washed 5 times with distilled water. The residue was dried, weighed and dissolved in the same manner as the untreated samples, and the filtrate was evaporated almost to dryness and subsequently dissolved in nitric acid. As not all the residue can be recovered from the filter paper the sum of the filtrate and residue values will not equal that of the original untreated sample, but replicate analyses of one sample per treatment serves as an indication of the reproducibility of the technique.

The acid/reducing treatment was carried out strictly according to Chester and Hughes (1967, p.258). Briefly, the method requires 1 g of samples to be shaken for 4 hours in 50 ml of a 35%(V/V) acetic acid/25%(V/V) hydroxylamine hydrochloride solution. After filtering, the residue and filtrate are dissolved in a similar manner as described above.

A third batch of the same samples was subjected to hydrogen peroxide treatment. Approximately 0,5 to 1,0 g of clay was added to 50 m, of 30% hydrogen peroxide in which a few drops of sulphuric acid had been placed (Gad and La Riche, 1966). Small quantities of hydrogen peroxide were added and slight heating was applied to the mixture until effervescence ceased completely. The filtrate and residue were treated as above.

Table AIII-3. Precision of atomic absorption technique compared to X-ray flourescence spectometry.

Sample	Element	X-ray flourescence			Atomic absorption							
		a	b	av.	10/2/1974		3/2/1975			av.	std. dev.	rel. dev.
					a	b	c	c	e			
R-21	Al	15,99	16,04	16,02	12,08	10,08	12,16	12,82	12,96	12,16	,86	7,07
	Fe	7,00	6,97	6,99	8,23	8,40	6,80	6,65	6,75	7,37	,87	11,80
	Ca	,48	,49	,49	,2	,6	,3	,4	,3	,36	,15	0,42
	K	3,45	3,45	3,45	2,10	2,15	1,96	1,99	2,02	2,04	,09	4,41
	Mn	,11	,12	,12	,07	,07	,08	,08	,08	,08	,01	12,50
	Ni	41	-	41	42	44	48	45	45	44,8	2,17	4,84
	Zn	104	-	104	50	58	52	54	60	54,8	4,15	7,57
	Pb	-	-	-	82	87	67	67	78	76,2	8,98	11,78
3320	Al	12,03	12,01	12,02	9,83	9,80	10,02	10,51	10,37	10,11	,32	3,17
	Fe	7,81	7,76	7,79	9,60	9,80	10,75	10,70	10,75	10,33	,58	5,61
	Ca	1,21	1,22	1,22	2,0	2,0	2,1	2,0	1,9	2,0	,07	3,50
	K	3,57	3,79	3,68	2,40	2,40	2,20	2,26	2,20	2,29	,10	4,37
	Mn	,12	,13	,13	,04	,04	,05	,05	,05	,05	,01	20,00
	Ni	52	-	52	63	64	50	50	48	55,0	7,81	14,20
	Zn	140	-	140	135	142	136	135	142	138,0	3,67	2,66
	Pb	-	-	-	76	82	71	70	68	73,4	5,64	7,68
3323	Al	11,44	12,01	11,73	8,35	8,50	8,80	8,60	8,60	8,57	,16	1,87
	Fe	6,85	7,76	7,31	7,20	7,22	8,85	8,60	8,70	8,11	,83	10,23
	Ca	1,82	1,22	1,52	,6	1,0	1,0	,8	,9	,86	,17	19,77
	K	3,21	3,79	3,50	2,00	2,00	1,94	1,84	1,78	1,91	,10	5,24
	Mn	,10	,13	,12	,03	,03	,03	,03	,03	,03	,00	,00
	Ni	89	-	89	88	90	80	80	78	83,2	5,40	6,49
	Zn	188	-	188	168	168	180	180	176	174,4	6,07	3,48
	Pb	-	-	-	63	63	50	56	46	55,6	7,64	13,74

Al, Fe, Ca, K and Mu in per cent; Ni, Zn and Pb in ppm.

(vi) Precision and accuracy.

During the contamination study (section B(i), 10 aliquots of one sample were dissolved and three machine read-outs of each analysis were recorded. This provided adequate information regarding the precision of the dissolution procedure (splitting, contamination, dilution, weighing errors, etc.), as well as the stability of the atomic absorption machine for the six elements studied.

This information was augmented by analysing river and marine sediments (R-21, 3320 and 3323) in replicate at the beginning and at the end of the study (one year apart). Subsamples were also analysed by X-ray fluorescence to give an indication of the accuracy of the analytical method (Table AIII-3).

The results of the above analyses indicate:-

(i) the atomic absorption machine is very stable for all elements analysed.

(ii) precision was best for Fe and Mn, whereas reproducibility for Zn and Pb was poor (Table AIII-3). This is due to the fact that the absorption for Zn and Pb are in the far ultra-violet region where entities in the flame absorb strongly.

(iii) the results of the atomic absorption analyses repeated a year apart were very similar to each other (Table AIII-3).

(iv) compared to the X-ray fluorescence analyses, the atomic absorption determinations were consistently low for Al, Ca, K and Mn, high for Fe, but Ni and Zn values were similar (Table AIII-3).

C(i) Semi-quantitative mineralogical analyses of the <2µm fraction

Sample number	% mont-morillonite	% illite	% kaolinite plus chlorite	% chlorite	$\frac{\text{chlorite}}{\text{illite}}$ (1)	crystallinity of mont-morillonite	$\frac{\text{alkali feldspar (1)}}{\text{plagioclase feldspar (2)}}$
104	9,6	77,5	13,0	0	-	0,40	-
108	11,3	80,7	7,9	0	-	0,50	-
287	18,1	72,3	9,5	0	-	0,42	-
297	9,0	81,4	9,6	2,2	0,04	0,56	0,69
298	5,1	80,6	14,3	1,6	0,03	0,50	-
300	8,2	77,5	14,3	2,1	0,04	0,50	0,40
309	23,7	54,1	22,2	2,0	0,06	0,76	-
311	9,2	80,9	9,7	1,6	0,03	0,64	-
330	1,2	94,3	4,5	1,9	0,03	0,53	-
1696	9,4	80,3	10,4	0,5	0,01	0,63	0,61
1700	16,0	58,3	25,7	1,2	0,03	0,58	-
1717	24,6	55,1	20,3	2,9	0,08	0,45	0,51
1720	17,9	71,5	10,6	1,3	0,03	0,60	0,66
2229	22,8	54,4	22,8	2,3	0,06	0,16	-
2239	8,2	85,9	6,0	0,5	0,01	0,75	-
2241	10,8	81,6	7,6	0,8	0,01	0,62	1,00
2244	10,5	82,2	7,2	1,2	0,02	0,58	0,60
2249	12,6	63,2	24,2	1,8	0,08	0,11	0,34
2265	20,2	59,6	20,2	2,4	0,06	0,46	0,40
2277	6,0	89,2	4,8	0	-	0,38	0,80
2278	24,5	69,9	5,6	1,8	0,04	0,35	-
2279	14,3	65,3	20,4	1,4	0,03	0,06	0,57
2281	24,0	60,0	16,0	2,7	0,07	-	-
2286	19,0	71,0	10,0	-	-	0,46	-
2290	9,6	77,0	13,3	0,6	0,01	0,06	-
2293	19,4	55,8	24,7	0	-	0,12	0,60
2294	9,4	87,5	3,1	0,3	0,01	0,33	-

Sample number	% mont-morillonite	% illite	% kaolinite plus chlorite	% chlorite	chlorite / illite (1)	crystallinity of mont-morillonite	alkali feldspar / plagioclase feldspar (1) (2)
2335	16,2	64,9	18,8	0,5	0,01	0,27	-
2339	18,0	62,1	19,9	0	-	0,25	-
2355	26,8	66,7	6,6	1,5	0,03	0,42	-
2357	19,3	69,6	11,1	2,2	0,05	0,26	-
2358	17,2	63,4	18,9	1,5	0,04	0,18	-
2359	17,9	71,7	10,3	1,3	0,02	0,10	-
2363	14,9	65,6	19,4	2,6	0,06	0,41	-
2365	28,4	61,1	10,5	0,9	0,02	0,40	0,80
2370	32,2	55,9	11,9	0,6	0,02	0,44	-
2373	12,1	75,8	12,1	1,6	0,03	0,54	-
2375	21,0	73,0	6,1	2,1	0,04	0,38	-
2377	35,9	55,8	8,3	1,8	0,05	0,31	0,86
2382	29,8	56,1	14,0	1,8	0,05	0,56	-
2440	23,1	71,8	5,1	0	-	0,50	-
2443	10,0	59,6	30,4	2,4	0,06	0,17	-
2446	3,9	91,9	4,23	0	-	0,40	0,61
2448	17,0	63,7	19,4	0	-	0,38	0,51
2450	10,7	64,3	25,0	0	-	0,29	-
2451	19,3	70,0	13,4	0,4	0,01	0,21	-
2454	11,8	71,1	17,1	3,9	0,08	0,09	-
2456	11,8	54,7	33,5	1,2	0,03	0,06	0,44
2459	14,5	67,9	17,6	1,3	0,03	0,12	-
2460	8,9	63,3	27,8	1,3	0,03	0,21	-
2464	16,0	63,9	20,2	1,1	0,01	0,13	-
2473	3,8	94,7	1,5	0,2	0,01	-	-
2488	14,8	78,5	6,7	0,5	0,01	0,28	-
2678	21,2	69,9	8,9	0,3	0,04	0,31	-

Sample number	% mont-morillonite	% illite	% kaolinite plus chlorite	% chlorite	chlorite / illite (1)	crystallinity of mont-morillonite	alkali feldspar / plagioclase feldspar (2)
2686	26,9	63,2	9,9	1,6	0,04	0,32	-
2691	8,0	87,0	5,0	1,2	0,02	-	-
2693	8,2	79,6	12,2	0,7	0,01	-	-
2696	28,8	53,9	17,8	1,5	0,03	0,67	0,57
2701	7,7	87,2	5,1	1,1	0,02	-	-
2702	8,2	84,2	7,6	-	-	0,31	-
2705	8,8	65,3	25,9	0,9	0,02	0,08	-
2710	16,0	66,0	18,1	2,6	0,06	0,47	-
2712	14,1	78,7	7,2	1,1	0,02	0,54	1,01
2716	8,1	84,2	7,7	2,2	0,04	0,31	-
2719	4,6	92,7	2,7	1,2	0,02	-	-
2759	2,3	91,0	6,8	2,6	0,03	-	-
2790	15,8	67,7	16,5	1,3	0,03	0,55	-
2798	18,2	65,8	16,0	2,9	0,07	0,44	-
2840	20,6	75,6	3,9	0,7	0,01	0,15	-
3085	10,9	76,4	12,7	1,9	0,04	0,61	-
3098	6,7	69,7	23,6	0,7	0,01	0,42	-
3107	22,9	69,8	7,2	0,7	0,02	0,48	-
3111	12,6	78,0	9,4	0,5	0,01	0,28	-
3117	30,6	60,5	8,9	0,4	0,01	0,63	-
3298	21,9	67,9	10,2	1,8	0,04	0,78	-
3302	29,1	54,3	16,6	1,1	0,03	0,58	-
3305	27,0	56,1	16,9	0,6	0,04	0,50	-
3308	44,8	42,6	12,6	1,4	0,05	0,50	-
3312	22,0	70,3	7,8	1,8	0,04	0,37	-
3320	4,0	86,8	9,2	0,9	0,02	0,48	-

Sample number	% mont-morillonite	% illite	% kaolinite plus chlorite	% chlorite	chlorite / illite (1)	crystallinity of mont-morillonite	alkali feldspar / plagioclase feldspar (1) (2)
3321	5,6	85,6	8,8	1,8	0,03	0,31	-
3323	9,4	82,2	8,3	1,7	0,03	0,29	1,00
3339	30,8	59,8	9,4	0,6	0,01	0,50	-
3341	27,1	66,7	6,2	0,9	0,02	0,52	-
3343	13,6	77,1	9,3	0,7	0,02	0,67	-
3345	19,7	43,5	36,7	0	-	0,44	-
3346	23,3	60,2	16,5	0,5	0,01	0,29	-
3350	29,1	63,7	7,2	0,7	0,02	0,69	-
R-1	0,0	81,6	18,4	0,5	0,01	-	-
-2	0,0	61,4	38,6	0	-	-	-
-5	0,7	30,7	68,7	0	-	0,12	1,42
-9	0,7	76,9	22,4	0	-	0,25	4,03
-12	3,4	91,9	4,7	0,5	0,01	-	-
-16	0,0	73,1	26,9	0	-	-	0,58
-20	0,0	63,7	36,3	0	-	-	-
-21	0,0	61,4	38,6	0,5	0,01	-	-
-23	5,6	85,3	9,1	0	-	0,51	1,48
-24	0,0	92,6	7,4	1,1	0,02	-	-
-31	2,8	83,3	13,9	0	-	-	-
-32	6,3	82,5	11,1	1,6	0,30	0,36	-
-33	3,9	85,0	11,1	1,7	0,03	0,01	0,03
-34	2,7	79,2	18,1	0	-	-	1,36
-36	23,8	30,7	45,5	0	-	0,48	1,70
-37	0,0	73,4	26,6	0	-	-	-

(1) ratios of peak areas
(2) no alkali feldspar present.

D(i) Geochemical analyses of the <2μm fraction

Sample Number	Aluminium %	Potassium %	Iron %	Manganese ppm	Calcium %	Nickel ppm	Zinc ppm	Lead ppm	Organic carbon %
(a) Marine clays:									
108	6,60	1,45	5,65	238	21,3	95	354	17	is[1]
287	5,70	1,02	4,12	161	15,1	110	214	24	6,2
298	7,78	1,58	4,32	203	19,5	88	-	26	6,2
300	2,42	1,37	4,38	179	26,0	77	233	23	4,5
309	4,33	1,04	3,94	153	18,9	83	370	62	is
311	5,13	1,25	4,14	169	27,5	80	315	106	is
330	4,94	1,26	4,60	163	32,0	85	340	106	is
1696	4,86	1,13	4,40	180	13,0	106	265	40	5,6
1700	6,00	1,50	5,63	270	22,5	108	445	10	is
1717	2,90	0,75	3,00	103	-	50	157	25	is
1720	6,15	1,43	5,23	199	15,0	107	355	26	3,1
2229	7,16	1,71	6,94	240	8,0	125	305	18	3,6
2239	5,64	1,30	5,38	222	5,8	120	448	48	is
2241	5,35	0,99	5,20	211	25,0	110	233	62	is
2244	4,95	1,04	5,32	166	24,3	127	301	89	is
2249	6,12	1,45	5,57	219	11,5	123	-	40	is
2265	5,48	1,13	5,18	173	33,0	128	205	15	is
2279	6,18	1,27	5,86	200	13,0	114	239	19	is
2290	6,13	1,53	6,87	204	8,5	125	339	63	3,7
2293	6,24	1,48	6,04	230	4,0	130	290	20	3,6
2335	6,38	1,40	5,98	200	9,5	145	407	123	is
2339	7,16	1,55	6,88	218	3,8	130	492	80	5,4
2358	6,65	1,35	6,65	211	3,8	136	438	97	is
2363	5,25	1,23	5,38	203	15,5	125	320	123	is
2370	5,20	1,13	4,78	358	10,3	127	200	25	is
2373	1,75	0,95	4,13	185	30,3	125	368	35	is

(1) is. Insufficient sample for analysis.

Sample number	Aluminium %	Potassium %	Iron %	Manganese ppm	Calcium %	Nickel ppm	Zinc ppm	Lead ppm	Organic carbon %
2377	6,66	1,28	6,17	258	14,3	140	178	5	is
2443	5,54	1,27	5,13	185	18,0	125	267	20	is
2446	3,97	0,98	3,94	163	28,5	103	325	20	is
2448	3,25	0,64	2,88	130	20,8	100	368	125	5,7
2450	3,45	0,68	2,93	150	39,0	83	250	23	is
2454	4,75	0,98	4,13	155	28,5	107	220	23	7,6
2456	3,80	0,87	3,37	158	19,5	87	213	67	is
2460	-	-	2,20	-	-	103	368	49	is
2678	5,73	1,27	5,13	188	23,5	125	209	10	4,3
2691	2,67	0,59	3,40	105	43,0	98	337	14	is
2696	-	0,43	2,04	83	51,0	64	198	36	3,3
2702	1,63	0,40	1,38	108	50,0	88	363	50	is
2705	2,75	0,72	2,53	124	36,5	100	350	130	is
2710	6,13	1,44	3,90	209	10,5	119	278	45	2,4
2712	8,14	1,65	8,86	251	2,0	77	143	29	2,4
2716	4,79	1,02	4,38	176	26,6	119	265	31	is
2790	7,35	1,67	6,45	233	15,5	118	246	32	4,3
2798	5,13	1,18	6,30	198	21,2	120	150	25	5,6
3085	8,05	1,92	6,20	250	4,6	89	317	55	is
3098	9,72	2,64	7,60	348	3,3	82	238	18	is
3107	2,16	0,62	2,02	79	27,1	75	131	64	is
3111	2,06	0,32	1,79	69	58,8	75	198	98	3,2
3117	2,17	0,38	2,19	93	54,2	45	193	111	1,3
3298	8,39	1,56	8,62	234	2,5	90	178	30	2,9
3302	8,02	1,52	8,96	231	1,9	94	231	18	2,0
3305	8,88	1,48	8,07	209	2,2	85	154	48	3,8
3308	7,64	1,40	9,16	227	4,2	121	235	20	3,6

Sample number	Aluminium %	Potassium %	Iron %	Manganese ppm	Calcium %	Nickel ppm	Zinc ppm	Lead ppm	Organic carbon %
3312	7,18	1,29	6,57	250	3,9	83	298	13	2,0
3320	9,83	2,40	9,70	424	2,0	64	139	79	3,8
3323	8,43	2,00	7,21	285	0,8	89	168	63	3,6
3339	3,13	0,60	1,63	112	54,3	51	108	58	2,5
3343	2,38	0,65	2,00	91	58,0	41	172	105	0,9
3345	2,17	0,40	1,93	78	52,8	65	215	107	is
3346	1,43	0,33	1,48	73	57,2	92	165	59	1,6
3350	2,56	0,70	1,47	95	51,4	50	113	64	1,2
Mean	5,29	1,18	4,87	188	21,8	99	281	48	3,6
Correlation matrix:									
Aliminium	-								
Potassium	,902	-							
Iron	,906	,844	-						
Manganese	,834	,878	,820	-					
Calcium	-,812	-,811	-,830	-,753	-				
Nickel	,311	,315	,398	,372	-,460	-			
Zinc	,116	,195	,054	,114	-,198	,395	-		
Lead	-,305	-,251	-,308	-,328	,313	-,255	,061	-	
Organ.Carbon	,026	,081	-,015	-,064	-,233	,597	,477	-,252	-
(b) River clays:									
R-2	9,30	1,76	4,58	280	1,7	34	92	70	0,8
-5	11,73	1,40	8,32	360	0,9	33	140	82	is
-9	11,74	1,83	8,90	450	0,5	37	177	79	is
-16	9,85	1,90	7,60	4175	0,9	37	129	41	is
-20	11,55	2,40	11,22	500	0,7	111	180	85	is
-21	11,44	2,13	8,29	275	0,4	54	101	85	is
-31	8,54	2,39	11,10	1800	0,3	43	215	68	is
-32	8,48	1,88	8,46	1326	1,8	50	158	55	0,8
-33	9,17	1,63	8,80	1150	2,2	61	116	57	is
-37	12,24	2,27	11,15	700	0,7	70	318	96	is
Mean	10,40	1,95	8,84	1101	1,0	53	162	71	0,8

D(ii) Results of element partitioning (1)(2)

Sample number	IRON (3)				MANGANESE				NICKEL				ZINC			
	untreated sample	filtrate ppm	filtrate %	residue	untreated sample	filtrate ppm	filtrate %	residue	untreated sample	filtrate ppm	filtrate %	residue	untreated sample	filtrate ppm	filtrate %	residue
I. GLACIAL ACETIC ACID TREATMENT																
R-32	856	43	5(4)	825(6)	1,326	600	45	705	50	0	0	50				
3323	646	15	2	660	258	28	11	246	89	0	0	86				
2448(a)	281	0	0	550	111	23	21	180	87	18	21	92				
(b)	281	0	0	575	111	29	26	188	87	22	25	92	see note (2)			
(c)	281	0	0	580	111	15	13	197	87	18	21	95				
3107	202	0	0	(5)	88	21	24	(5)	68	14	21	(5)				
II. ACID/REDUCING REAGENT																
R-32(a)	856	67	8(4)	740(6)	1,326	1,100	83	403	50	15	30	55				
(b)	856	68	8	740	1,326	1,250	94	430	50	10	20	55				
(c)	856	68	8	736	1,326	1,200	91	425	50	10	20	55				
3323	646	18	28	600	258	13	5	265	89	9	10	86	see note (2)			
2448	281	10	4	(5)	111	28	25	(5)	87	25	29	(5)				
3107	202	8	4	(5)	88	25	28	(5)	68	28	41	(5)				

Sample number	IRON[3]				MANGANESE				NICKEL				ZINC			
	untreated sample	filtrate ppm	filtrate %	residue	untreated sample	filtrate ppm	filtrate %	residue	untreated sample	filtrate ppm	filtrate %	residue	untreated sample	filtrate ppm	filtrate %	residue
III. GLACIAL ACETIC ACID DISSOLUTION FOLLOWED BY HYDROGEN PEROXIDE TREATMENT.																
(a) Glacial acetic acid dissolution																
R-32	856	40	5[4]	(5)	1326	242	41	(5)	50	0	0	(5)	158	13	8	(5)
3323(a)	646	25	4	(5)	258	28	11	(5)	89	8	9	(5)	168	46	27	(5)
(b)	646	25	4	(5)	258	28	11	(5)	89	9	10	(5)	168	47	27	(5)
(c)	646	25	4	(5)	258	27	11	(5)	89	8	9	(5)	168	47	27	(5)
2448	281	5	2	(5)	111	32	29	(5)	87	15	17	(5)	368	99	27	(5)
3107	202	1	0,5	(5)	88	13	15	(5)	68	22	32	(5)	131	43	33	(5)
(b) Hydrogen peroxide treatment on above residues.																
R-32	997	347	35[7]	650	660	492	75	168	59	34	58	25	141	65	46	76
3323(a)	980	137	14	844	266	78	29	188	93	55	58	38	151	57	38	94
(b)	975	130	13	845	246	66	27	180	94	58	62	36	162	59	36	103
(c)	936	131	14	805	263	84	32	179	96	57	59	39	159	64	40	95
2448	929	304	33	625	222	117	53	105	135	122	90	13	311	180	58	131
3107	922	265	29	657	250	128	51	122	126	96	76	30	246	172	70	74

NOTES: (1) All values in ppm (g/μg)

(2) Pb was omitted from the partitioning study because of poor precision and Zn was excluded in the first two treatments owing to excessively high blank determinations.

(3) Values $x10^2$

(4) Expressed as a percentage of the untreated sample content.

(5) Insufficient sample for analysis.

(6) The sum of the "residue" and "filtrate" will not equal that of the "untreated sample" because the composition of the residue will have changed during treatment (e.g. the carbonate phase is removed by the acid treatment, thereby enhancing the metal content).

(7) Because of insufficient material, determinations were not made of every glacial acetic acid and acid/reducing reagent residue. The trace metal content of the material prior to the second treatment was therefore sometimes unknown. The proportion of elements liberated during the subsequent process was thus calculated as a fraction of the sum of the filtrate and residue contents of the second treatment.

(8) These values are (see (7) above) the sum of the filtrate and residue determinations.

APPENDIX IV - ANALYSES OF PHOSPHATIC AND GLAUCONITIC MATERIALS

IV - A. Classification and composition of phosphorite rocks.

(i) Location, depth, weight and the class of phosphorite rock recovered at each station.

(ii) Brief hand specimen descriptions, thin section analyses and chemical data (P_2O_5, K_2O).

IV - B. Whole rock and microprobe analyses of phosphatic and glauconitic materials: Methods and results.

(i) Methods.

(ii) Results of whole rock analyses of onland and off-shore phosphorites.

(iii) Location and description of materials analysed using the electron microprobe.

(iv) Results of microprobe analyses of off-shore phosphorites and glauconites.

(v) Results of microprobe analyses of onland phosphorites.

(vi) Micro-analyses of phosphorite cements, phosphate grains and pelletal phosphorites (see section 4.4.9.(c)).

IV - C. X-ray diffraction determinations of CO_2 in the apatite phase of off-shore and onshore phosphatic material.

IV - A. Classification and composition of phosphorite rocks.

A(i) - Location, depth, weight and class of phosphorite rocks recovered at each station.

(a) Phosphorite and limestone recovered by the Marine Geology Unit, U.C.T.

STATION NUMBER	POSITION				DEPTH (m)	WEIGHT (kg)	PHOSPHORITE CLASS
	LATITUDE (South)		LONGITUDE (East)				
	deg.	min.	deg.	min.			
310	34	42.8	18	08.8	376	>100	(A)CI:(B)NIIIA;(C)NI
313	34	34.5	18	05.0	340	25	(A)CI;(C)NI;(B)shell
314	34	25.5	17	40.0	770	<1	(A)NIIIB
1686	34	49.0	19	02.3	150	10	GPL
1692	34	36.0	18	22.0	320	9	(B)NIIIB;(C)NII/NIIIA
1700	34	38.3	18	06.3	345	>100	(A)NIIIA;(B)CI
1701	34	32.0	18	10.0	310	9	(A)NIA;(B)CI;(E)NIA
1702	34	24.0	18	12.6	293	14	(A) and (C)NIIIB
1703	34	19.0	18	17.5	120	1	NIIIA
1705	34	20.0	18	07.0	260	1	NIIIA
1706	34	20.7	18	58.8	305	61	(B) and (D)NI;(C)CI
1709	34	18.0	17	53.0	310	2	(C)NIA
1714	34	07.5	17	56.5	240	<1	NIIIA
1717	33	46.5	17	39.0	265	1	(A)NIIIA;(B)bone
2210	33	32.0	18	15.0	45	3	(D)lmst
2217	33	22.0	17	37.0	320	31	(A)NIIIB
2219	33	08.0	17	15.0	420	18	(B)NIA;(D)NIA;(E)CI;(Fi)IIIA/ NIIIA(Fii)CI;(G)NIIIA
2220	33	08.0	17	30.0	350	52	(A)NIIIA;(E)NIIIB;(F)NIIIB;(G)NIA
2230	33	12.7	17	30.0	420	41	(A)NIIIA;(C)CI;(D)bone
2231	33	11.0	17	23.0	380	<1	CI
2239	33	00.0	17	33.0	305	14	NIIIB
2240	33	01.0	17	25.0	310	42	(A)CI;(B)NIA
2241	33	02.0	17	14.0	355	<1	CI
2245	32	51.0	17	03.0	355	5	(C)bone;(D)NIIIA
2246	32	49.0	17	13.0	315	2	NIA
2247	32	50.0	17	22.0	300	1	(A)CI;(B)GPL;(C)NIIIA;(D)NIA
2248	32	49.0	17	25.0	280	4	(A)GPL;(B)NIIIA;(C)GPL
2254	32	53.2	17	28.0	270	20	(A)GPL;(C)CII/NIIIA;(D)NIIIA
2266	32	32.5	16	49.5	330	<1	(A)NIA;(B)NI/NIIIA
2274	32	32.5	18	12.0	37	1	(B)lmst
2275	32	34.2	18	17.4	15	1	(A)lmst
2285	32	33.5	16	30.5	650	<1	(A)NIA;(B)NIA
2361	31	18.8	16	51.5	459	17	(A)NIB;(C)lmst;(D)CI/NII
2369	31	09.2	17	13.8	192	<1	NIA
2437	33	51.0	17	27.5	398	<1	(B)NIIIA;(C)bone
2449	31	41.5	16	17.5	388	9	(A)CI/CII;(C)NIA
2460	31	14.0	16	37.5	275	22	NIIIA/CII
2461	31	19.0	16	41.0	270	<1	NI
2462 (grab)	31	19.0	16	10.0	320	<1	NIIIB
2462 (dredge)	31	19.0	16	10.0	320	<1	CII
2463	31	08.5	16	22.8	300	<1	NIA
2468	30	57.0	15	35.0	299	<1	(A)NIB;(B)NIB
2483	30	55.0	16	24.5	271	1	(A) and (B)NIA/GPL

STATION NUMBER	POSITION LATITUDE (South) deg.	min.	LONGITUDE (East) deg.	min.	DEPTH (m)	WEIGHT (kg)	PHOSPHORITE CLASS
2486	30	55.0	15	48.0	195	2	CII
2487	30	55.0	15	36.7	262	<1	(A)NIB;(B)CII
2495	30	35.0	16	38.0	222	30	(A)(i)+(ii)lmst;(B)NIIIB
2688	30	30.0	16	11.0	243	2	(A)(i)lmst;(ii)NIA;(B)NIA
2703 (grab)	30	08.0	15	26.0	210	<1	NIA
2703 (dredge)	30	08.0	15	26.0	210	<1	NIA
2716	30	23.0	16	38.0	198	<1	(A)NIA;and(B)NII
2718	30	25.0	16	15.0	225	<1	NIA
2786	33	13.5	17	29.0	420	1	CI
2841	31	00.0	15	45.0	295	3	(A)NIA;(B)NIB;(C)NIA;(D)NIA
2842	30	58.0	15	44.0	250	<1	(A)lmst;(B)NIA;(C)lmst
(b) Non-MGU phosphorites, limestones and phosphatized bone.							
GiL-674	34	24.7	18	20.6	187	2	NIA
GiL-675	34	13.0	17	46.0	366	7	(D)NIA;(E)NIA;(F)NIA
A.5194	32	27.0	16	50.0	350	10	(A)NIA;(B)NIA
A.5407	34	27.0	17	53.0	384	12	(A)NIA;(B)CI;(C)(D)bone
A.5828	33	45.0	17	42.0	219	15	(A)phos bone(B)unphos bone
A.5836	33	43.0	17	29.0	457	25	phos bone
A.5837	33	46.0	17	25.0	530	2	phos bone
A.5838	33	53	17	24.0	640	35	lmst
F1A	33	46	17	29.0	402	±30	(A)phos whale bone;(B)unphos whale bone

A(ii) Brief hand specimen descriptions, thin section analyses and chemical data (P_2O_5, K_2O).

The phosphorites have been listed by regions and by classes below. Abundances were estimated visually using diagrams by Terry and Chilingar (1955) and point-count determinations were made on a representative number of thin sections to check the estimates, with satisfactory results. Figures within parenthesis above the values obtained by estimation indicate abundances obtained by point-counting 300 or more grains per slide. Wherever two symbols are presented the first indicates the more abundant component.

Abbreviations used:

Under glauconite
size: S = small <0,15 mm
M = medium 0,15-0,35 mm
L = large >0,35 mm

shape: S = secondary morphology (well rounded, non-sutured)
P = primary morphology (highly sutured, lobate)

mottl.: = mottled admixture of apatite and glauconite

oxid.: = oxidized grains

rims: = apatite rim

Under forams
P = prominant (>50%)
V = common (5-50%)
M = minor (<5%)

Under chemistry
ts = too small for chemical analyses

Under cement and pebbles (conglomeratic classes only)
matrix: mixture of silt- and sand-size grains and cement, but excludes the pebbles.

Under cement
cement: Intergranular mixture of collophane, micrite, glauconite or goethite which cements the detrital grains together.

M : Micrite
C : Collophane
Gl: Glauconite
Go: Goethite

LIMESTONES (<5% P_2O_5)

SAMPLE NUMBER	HAND SPECIMEN DESCRIPTION	PETROGRAPHIC ANALYSIS													CHEMISTRY		
		GLAUCONITE							FORAMS					COMMENTS			
		%	size	shape	mottl	rims	oxid	% quartz	%	plank benth	filled	macrofos	cement		P_2O_5	K_2O	P_2O_5/K_2O
	(a) Cape Peninsula Region																
2210D	V lt gry rnded cobbles of fine-graind lmst													No thin sect.High %age qz,possibly a calcareous siltst.	2,3	0,49	4,69
A5838	V pl oran large cobbles fine-graind lmst.	<1	M	S	M	O	O	50	O	-	-	O		MCalcareous siltst.	1,8	1,05	1,71
	(b) Saldanha Bay Region																
2274B	V lt gry shelly,v crse pebbles,friable lmst.													No thin sect.	3,0	0,53	5,66
2275A	V lt gry fine-grained porous rnded crse pebbles lmst.													No thin sect.	3,8	0,34	11,17
	(c) Childs Bank Region																
2361C	V lt gry cobbles of algal nodules or rnded lmst frag.	<1	S	S	O	O	O	<1	<5	P	O	P		Coraline algae,bryozoa, forams Mmicrite	4,4	0,15	29,33
2495A(i)	Yelish gry to olv gry v irreg tabloid cobbles with pitted (?)phosd surf.	O	-	-	-	-	-	O	O	-	-	P		Macrofossils with Mmicrite cement	2,00	0,07	28,57
A(ii)	V lt gry poorly consolidated fine-graind lmst or mudst													No thin sect.layered with A(ii)	0.6	0,03	19,00
2688A(i)	V lt gry porous poorly consolidated fine-graind lmst cobbles													No thin sect.	2,0	0,19	10,26
2842A	Pl yelish brn to yelish gry rnded large cobbles with rough surf	<1	S	?P	O	O	O	O	>50	P	M	O		Forams filled with M,C?phos	2,3	0,09	25,55
														AVERAGE FOR LIMESTONES	2,5	0,33	15,10

GPL CLASS LIMESTONES

SAMPLE NUMBER	HAND SPECIMEN DESCRIPTION	PETROGRAPHIC ANALYSIS													CHEMISTRY		
		GLAUCONITE						% quartz	FORAMS			macrofos	cement	COMMENTS	P_2O_5	K_2O	P_2O_5/K_2O
		%	size	shape	mottl	rims	oxid		%	plank benth	filled						
(a) Cape Peninsula Region																	
1686	Yelish gry irreg porous poorly consolidated lge cobbles with macrofossils	5	M	S,P	M	M	M	15	10	B,P	M	PM,C		Forams filled with gl.	4,9	1,43	3,42
(b) Saldanha Bay Region																	
2247B	P1 olv irreg v crse pebbles with porous surf and pecten shells	50	S,L	S,P	P	O	P	<5	0	O	O	PM,C		Oxidized gl grains distinctive	ts	ts	ts
2248A(i)	P1 olv irreg v crse pebbles with porous rough surf enclsg small phos pebbles	(16) 15	M	S	P	O	O	(12) 10	(05) 0	-	O	(12) PM,C	(60)	Phos pebbles present. pebbles of highly qzitic phos.	ts	ts	ts
(ii)	Sim to 2248A(i),but enclosg pecten shells not phos pebbles	10	M	S	P	O	P	5	0	-	O	PM,C			11,9	1,44	8,26
2248C	Yelish gry rnded fine-grained v crse pebble with gritty surf	5	S,M	?P	O	O	O	20	0	-	O	OM,C		Different variety of gl to 2248(B) Felspar present	ts	ts	ts
2254A	Dsky yel porous irreg v crse pebbles & rough surf.	10	M	S	P	V	P	15	5	P,B	M	PM,C		Echinoderm & pecten shells.Inclusions of qz-rich phos pebbles. V small qz & felspar grains	6,4	1,47	4,35
														AVERAGE FOR GLAUCONITIC PHOSPHATIZED LIMESTONES	7,7	1,45	5,34
(c) Childs Bank Region																	
	None																

NIA CLASS PHOSPHORITES AND LIMESTONES

SAMPLE NUMBER	HAND SPECIMEN DESCRIPTION	PETROGRAPHIC ANALYSIS													CHEMISTRY		
		GLAUCONITE							FORAMS								
		%	size	shape	mottl	rims	oxid	% quartz	%	plank benth	filled	macrofos	cement	COMMENTS	P_2O_5	K_2O	P_2O_5/K_2O
(a) Cape Peninsula Region																	
310C	Yel gry rnded crse pbles	0	-	-	-	-	-	<5	15	P	0	0	M	Tending to ?phosphatise around boring Choles.minor bryozoa	18,4	2,59	7,10
313C	Yel gry porous small cobbles, showg increasd phos towards edges	<1	S	S	0	0	0	5	5	P	G	0	M,C		15,8	1,13	13,98
1701E(i)	Yel gry irreg v crse pbles & cobbles with pitted surf.	0	-	-	-	-	-	<1	1	P	0	V	M,C		15,8	1,44	10,97
E(ii)	Same	<1	S	S	0	0	0	<5	7	P,B	0	V	M,C				
1706B&D	Yel gry to yel olv gry v irreg med pbles to large cobbles pitted surfs.													Mainly micrite. Bryozoa rare. Other unident. macrofos.	(B)15,1	1,19	12,66
	1706(D) dker & more phos than (B)	(1) <1	S	S	0	0	0	(2)(10) 1	<5	P,B	M	(0) M	(87) M,C	pres. Secondry gln in cracks	(D)16,9	0,91	18,57
1709C	Dsky yel irreg ovoid v crse pbles													No thin sect.	22,7	0,92	24,67
GiL-674	Yel gry rnded v crse pbles rough surf	(5) 1	L	S	P	0	V	(5)(1) 1	<5	P	P	0	(89) G,C,M	Matrix glaucontzd but forams preferentially so	19,4	1,13	17,16
GiL-675D	Yel gry tabloid med cobble with enclosed macrofossils													Sim to GiL-674 No thin sect.	18,0	1,13	15,92

NIA CLASS PHOSPHORITES (Continued)

SAMPLE NUMBER	HAND SPECIMEN DESCRIPTION	PETROGRAPHIC ANALYSIS													CHEMISTRY		
		GLAUCONITE						% quartz	FORAMS			macrofos	cement	COMMENTS	P_2O_5	K_2O	P_2O_5/K_2O
		%	size	shape	mottl	rims	oxid		%	plank benth	filled						
GiL-675E	Gryish yel highly irreg crse pbls													No thin sect.	18,0	1,13	15,92
F	Yel gry ovoid med pbles													No thin sect.	11,0	1,64	6,70
A54L7A	Lt olv gry irreg cobbles with slightly bored surf.													No thin sect.	21,4	0,77	27,79
														Average	17,5	1,27	15,58
(b) Saldanha Bay Region																	
2219B	Yel gry v crse angular fine-grained fragmts.(ii) dker & more phos^{d} than (i)	1	S	?P	0	0	0	<1	25	P	M	O	G,M,C	Cement partially glaucnzd (i) forams & fillgs preferentially so(ii)	20,5	0,88	23,29
															21,6	1,00	21,6
D	Lt olv gry ovoid med to lge cobbles with smooth surf.	(2) 5	S	P	0	0	0	(8) 5	(5) 15	P	P	O	(85) G1		21,5	1,06	20,28
2220G	Yel gry irreg rnded v crse pbles fine-grained	<1	S	S	0	0	0	1	30	P	P	O	M,C	Agglutinated forams present	ts	ts	ts
2240B	Yel gry v irreg rnded v crse pbles fine-grained with borings													No thin sect.	12,3	1,30	9,46
2246	Yelish gry irreg cobbles with bored cavities													No thin sect.	15,3	0,71	21,85
2247D	Lt olv gry ovoid v crse pbles	<1	S	S	0	0	0	<1	30	P,B	V	O	M,C		17,8	1,05	16,95
2266A	Yel gry irreg v crse pbles showg phos^{n} towards edge	5	S	S	?	0	0	<1	25	P,B	M	O	M,C		16,0	0,99	16,16

NIA CLASS PHOSPHORITES (Continued)

SAMPLE NUMBER	HAND SPECIMEN DESCRIPTION	PETROGRAPHIC ANALYSIS													COMMENTS	CHEMISTRY		
		GLAUCONITE						% quartz	FORAMS			macrofos	cement			P_2O_5	K_2O	P_2O_5/K_2O
		%	size	shape	mottl	rims	oxid		%	plank benth	filled							
2285A	Yel gry rnded porous crse pbles	0	-	-	-	-	-	<1	50	P	0	0	M,C			14,5	0,78	18,58
B	Yelish brn irreg v crse pbles with rough surf.	<5	S	S	?	0	0	<5	40	P	0	0	M,C			21,9	0,63	34,76
A5194A	Yelish gry irreg large pbles with pitted surf.														No thin sect. Not	22,7	0,54	42,03
B	Yelish gry large pbles of fine-graind (?)lmst.														plotted as location is doubtful	18,6	0,47	39,57
															Average	16,4	0,86	24,05
(c) Childs Bank Region																		
2449C	Gryish yel tabloid lge cobbles porous fine-grain ed rough surf.	<5	S	S	M	0	0	<1	20	P,B	P	0	M,C		Forams filld with? goethite.Sim to GPL but less & smaller gl.& qz.	10,3	0,87	11,83
2461	Mod yel brn ovoid lge cobbles smooth surfaced with lge rnd cavities	(0.5) 0	-	-	-	-	-	(o) (8) 0	(3) 10	P, B	P	P	(72) C,M, Go		Forams filld with ? goethite/gl(9).Echi-noids(2),Bryozoa(1) Sim to 2716B	26,0	0,26	100,0
2463	Pl yelish brn highly ir-reg cobbles lge cavities & bored surf.	<1	S	S	0	0	0	0	40	P,B	P	0	M,C		Forams filled with gl.&?goethite	18,6	0,86	21,62
2688A(ii)	V lt gry porous poorly-consolidated fine-grained lge cobbles	5	S	S,P	V	0	0	<1	5	P	V	0	M,C		Foram tests common-ly replaced by opa-que (?Fe) min.	7,8	0,16	48,75

NIA CLASS PHOSPHORITES (Continued)

SAMPLE NUMBER	HAND SPECIMEN DESCRIPTION	PETROGRAPHIC ANALYSIS													CHEMISTRY		
		GLAUCONITE						% quartz	FORAMS			macrofos	cement	COMMENTS	P_2O_5	K_2O	P_2O_5/K_2O
		%	size	shape	mottl	rims	oxid		%	plank benth	filled						
2688B	Olv gry irreg small cobbles with smooth surf.	(11) <5	S	S,P	?0	0	0	(1) <1	(7) 10	P,B	0	<1	(81) C,G	Matrix partially gla luconitizd.Foram tests commonly replaced by opaque (?Fe) min.	18,5	-	-
2703(grab)	Yelish gry irreg small cobbles,smooth surf, lge cavities	(0) 0	-	-	-	-	-	(0) <1	(46) >50	P	P	0	(54) M,C	Forams filld with phos/?goethite(14)	ts	ts	ts
2703 (dredge)	Dsky yel irreg small cobbles,smooth surf, lge cavities													No thin sect.	19,9	0,34	58,52
2716A	Yel gry large cobbles, porous, fine-grained													No thin sect	5,0	0,13	38,46
2718	Yel gry small cobbles, porous, fine-grained	<5	S	S,P	0	0	0	<1	20	B,P	M	0	M,C	Forams filld with gl. or phos.	12,3	-	-
2841A	Pl yelish brn rnded lge pebbles with rough surf.	<1	S	S	0	0	0	0		P	M	?	MC	Mainly foram frags, goshell debris,micrite	16,4	0,17	96,47
C	Yelish gry irreg lge tabloid cobbles	<1	S	S	0	0	0	0	5	P	M	V	M,C	Bryozoa pres.Sim to 2841(A) Minor Fe-rich matrix	21,4	0,43	49,76
2841D	Med gry rnd cobbles with smooth surf	0	-	-	-	-	-	0	10	P,B	V	0	M,C	Fe-rich matrix	-	-	-
2842B	Med gry with lt gry inclusions rnded lge cobbles, rough surf	<1	S	?P	0	0	0	0	>50	P	M	0	M,C	Minor forams filld with ?phos	7,8	0,16	48,75
															12,9	0,35	46,69

NIB PHOSPHORITE CLASS

SAMPLE NUMBER	HAND SPECIMEN DESCRIPTION	PETROGRAPHIC ANALYSIS													CHEMISTRY		
		GLAUCONITE						% quartz	FORAMS			macrofos	cement	COMMENTS	P_2O_5	K_2O	P_2O_5/K_2O
		%	size	shape	mottl	rims	oxid		%	plank benth	filled						
2361A	Yelish gry v irreg tabloid cobbles lge cavities porous surf.	<1	S	S	O	O	O	O	<1	P,B	V	V	M,C	Coraline algae, bryozoa common	15,9	0,37	42,97
2369	V lt gry angular v crse pbles fine-grained porous surf	O	-	-	-	-	-	O	O	-	-	V	M,C	Mainly bryozoa & micrite	11,1	0,31	35,80
2468A	Pl yelish brn, angular cobbles, slightly layerd	<1	S,M	S	V	O	O	<1	±10	P,B	O	O	M,C,G	Coraline algae & bryozoa fragmts present	11,0	0,20	55,00
2468B	Dsky yel irreg small cobbles with rough surf	<1	S	S	O	O	O	O	<1	P,B	O	P	M,C,G	Coraline algae fragmts common Interstitial ? apatite	22,7	0,30	75,66
2487A	V pl oran tabloid small cobbles, porous, fine-grained, bored surf	O	-	-	-	-	-	O	O	-	-	M	M,C	Mainly micrite. Coraline algae & bryozoa present	5,7	0,10	57,00
2841B	Med gry with lt gry inclusions rnded lge pbles rough surf	O	-	-	-	-	-	O	O	-	-	P	M,C	Echodermata, bryozoa & coraline algae present	21,0	0,21	100.00
														AVERAGE FOR NIB PHOSPHORITES	17,7	0,27	68,41
														AVERAGE FOR CHILDS BANK REGION	14,1	0,33	52,89
														GRAND AVERAGE FOR NI PHOSPHORITES	15,7	0,78	32,68

NII CLASS PHOSPHORITES

(a) (b) Cape Peninsula and Saldanha Bay Regions

None

NII CLASS PHOSPHORITES

SAMPLE NUMBER	HAND SPECIMEN DESCRIPTION	PETROGRAPHIC ANALYSIS													CHEMISTRY		
		GLAUCONITE							FORAMS					COMMENTS			
		%	size	shape	mottl	rims	oxid	% quartz	%	plank benth	filled	macrofos	cement		P_2O_5	K_2O	P_2O_5/K_2O
(c) Childs Bank Region																	
2716 B	Yel gry to med gry highly irreg cobble-size knobby with macrofossils	0	-	-	-	-	-	0	<5	B	0	P	Go,M	Mainly cement, no gl or qz. Sim to 2461	16,7	0,38	43,94
														AVERAGE FOR NII PHOSPHORITES	21,4	0,32	71,97

NIIIA CLASS PHOSPHORITES

(a) Cape Peninsula Region																	
310B	Gryish grn irreg v crse pebbles	40	L	S	P*	V	O	5	0	0	0	0	C	*Probably all of the grains	19,1	2,39	7,99
1700A	Lt olv gry irreg small cobbles rough surf with lge cavities	(30) 25	L	S	P	V	O	(6) 5	(3) <5	P	0	(0) 0	(58) C,M	No thin sect. Probably sim to comment of 1700B	19,1	1,25	15,28
1701A	Lt olv gry irreg medium pbles	30	L	S	P	V	O	3	<1	P	0	0	C,M	Phos grains common (2)			
1703	Olv gry ovoid crse pbles smooth surf	15	M,L	S(P)	P	V	O	5	<5	P,B	0	0	C,M	Rock fragmts >2,0mm in damter. Componts v much out of hydrolic equilibrium	18,4	2,28	8,07
1705B	Yel gry ovoid med pbles smooth surf	<5	M	S	V	O	M	<5	10	P,B	0	0	C,M	Sim to 1703 but less gl & smallr qz	ts	ts	ts
1714	Yel gry irreg ovoid med to crse pbles	(7) 7	S	S	P	V	O	(7) 10	(21) 20	P	M	0	M,C	(65) Unusually high foram content	17,8	2,59	6,87
														AVERAGE (excluding 2437B)	18,8	1,85	11,32

NIIIA CLASS PHOSPHORITES (continued)

SAMPLE NUMBER	HAND SPECIMEN DESCRIPTION	PETROGRAPHIC ANALYSIS													CHEMISTRY		
		GLAUCONITE							FORAMS					COMMENTS			
		%	size	shape	mottl	rims	oxid	% quartz	%	plank benth	filled	macrofos	cement		P_2O_5	K_2O	P_2O_5/K_2O
(b) Saldanha Region																	
2219G	Gryish blue grn ovoid crse pble rough surf.	(55) >50	L	P,S	P	V	O	(3) 5	(0) 0	-	-	-	(42) C		ts	ts	ts
2220A	Olv gry highly irreg med cobbles with knobbly surf													No thin sect	15,9	3,43	4,63
2230A	V. sim to 2254(D) below	>50	L	S(P)	P	P	O	<1	0	0	0	0	C	Phos grains present	16,8	3,16	5,31
2245D	Olv gry v irreg angular v crse pbls rough surf	15	M	S	P	V	O	<1	<1	P	0	0	C,M		21,5	1,9	11,31
2247C	Lt olv gry to olv gry rnd med pebbles													No thin sect	ts	ts	ts
2248B	Dusky yel grn ovoid crse pbles rough surf	>50	L	S(P)	P	P	O	<1	0	0	0	0	C	Phos grains present	20,0	2,71	7,38
2254D	Dsky yel grn ovoid irreg small cobbles with rough surf	(54) >50	L	S(P)	(72) P	(20) P	O	(1) <1	0	0	0	0	(45) C	No phos grains present	17,4	3,39	5,13
														AVERAGE	18,3	2,92	6,75
(c) Childs Bank Region																	
2495B	Olv gry small rnded cobbles, v smooth polished surf with small pble inclusions	(8) 5	S	S	O	O	M	(3) <1	10	-	-	O	(59) C	Collo characteristically colourless ?goethite/phos infillings (22)	24,4	0,89	27,41
2462 (grab)	Dk yel brn irreg crse pebbles with smooth surf	15	M	S	P	V	O	1	<5	P	P	O	C,M	Lge no. of phos grains & frags from associated CII phos	ts	ts	ts
														GRAND AVERAGE FOR NIIIA PHOSPHORITES	19,5	2,22	10,67

NIIIB CLASS PHOSPHORITES

SAMPLE NUMBER	HAND SPECIMEN DESCRIPTION	PETROGRAPHIC ANALYSIS													CHEMISTRY		
		GLAUCONITE							FORAMS					COMMENTS			
		%	size	shape	mottl	rims	oxid	% quartz	%	plank benth	filled	macrofos	cement		P_2O_5	K_2O	P_2O_5/K_2O
(a) Cape Peninsula Region																	
314A	Gryish yel grn crse angular pebbles	(25) 20	M	S	P	V	O	(3) 5	(2) 5	P	O	O	(68) C,M	Phos grains(2) & minor felspar.In some parts micrite & forams have not been replaced by collo	18,4	1,36	13,52
1692B	Lt olv gry highly irreg v crse pebbles rough surf with cavities	10	M	S	V	V	O	15	0	-	-	O	C	Phos grains,rk frags gl foram infillgs. pres.Pebbles sim to cement but some have a gl or micrite matrix	16,6	1,39	11,94
1702A&C	Yel gry irreg ovoid v crse pebbles & cobbles	20	L	S,P	P	V	P	20	<1	B,P	O	M	C	Pebbles have sim comp to cement	15,5	2,54	6,10
														AVERAGE	16,8	1,76	10,52
(b) Saldanha Bay Region																	
2217A	Pl yel brn to lt olv gry v irreg small cobbles v pitted rough surf	15	M	S	P	V	O	40	0	-	-	O	C	Phos grains pres.Sim to 2437B but gl more abundant	14,2	1,82	7,82
2220E	Pl grnish yel to yel gry v crse pebbles with gritty cement.Cement is lt gry low in gl & contains small gl-free phos pbles	(3) <5	S,L	S	M	O	V	(17) 20	(11) 10	P,B	O	O	(69) C,M	Large angular qz grains assocd with unbroken dilicate forams	16,2	1,03	15,72
2220F	Sim to 2220E, but both cement & pebbles are glic	15	S,L	S	P	V	O	10	<5	P	O	O	C,M		16,7	2,68	6,23

NIIIB CLASS PHOSPHORITES (Continued)

SAMPLE NUMBER	HAND SPECIMEN DESCRIPTION	PETROGRAPHIC ANALYSIS													CHEMISTRY		
		GLAUCONITE						% quartz	FORAMS			macrofos	cement	COMMENTS	P_2O_5	K_2O	P_2O_5/K_2O
		%	size	shape	mottl	rims	oxid		%	plank benth	filled						
2239	Lt olv gry irreg ovoid large cobbles	(18) 10	L,S	S,P	P	V	M	(21) 15	(1) <1	P,B	0	M	(59) C	Extremely poorly sortd.Lge(>4mm)qz, jasper,chalcedony grains,felspars & rk frags unevenly distributd in the rk.Phos grains are present(1)	15,5	1,91	8,11
														AVERAGE	15,7	1,85	9,47

(c) Childs Bank Region

None

														GRAND AVERAGE FOR NIIIB PHOSPHORITES	16,2	1,82	9,92

CI CLASS PHOSPHORITES

(a) Cape Peninsula Region

310A	Dsky yel oran to gry yel grn tabloid lge cobbles	(15)						(16)	(0)				(66)	Felspar & phos grains pres(2)	18,9	1,65	11,65
	Matrix	15	M	S	P	V	0	10	0	-	-	0	C,Gl				
	Pebbles	1	S	S	?	0	0	15	20	P	0	0	C,Gl	Typ NItype phos			
313A	Same as 310A																
	Matrix	20	M	S	P	V	0	<5	<5	P	0	0	M,C	Felspar & phos grains present	18,7	1,93	9,68
	Pebbles	<1	S	S	0	0	0	1	10	P	0	0	M,Gl				
1700B	Lt olv gry irreg small cobbles with cavities & rough surf													Felspar & phos grains present			
	Matrix	10	M	S	P	V	0	15	0	-	-	M	C	Other pbles sim to cement,but are par tially glized or phosized	20,4	1,82	11,20
	Pebbles	<1	L	S	?	0	0	<1	10	P	0	0	M,C				
	Pebbles	1	L	S	?	0	0	20	0	-	-	-	C				

CI CLASS PHOSPHORITES (Continued)

SAMPLE NUMBER	HAND SPECIMEN DESCRIPTION	PETROGRAPHIC ANALYSIS													CHEMISTRY		
		GLAUCONITE							FORAMS					COMMENTS			
		%	size	shape	mottl	rims	oxid	% quartz	%	plank benth	filled	macrofos	cement		P_2O_5	K_2O	P_2O_5/K_2O
1701B	Yelish gry to lt olv gry ovoid small cobbles													No thin sect. but sim to 1700B	18,3	2,13	8,59
1706C	Yelish gry to olv gry tabloid lge cobbles enclosg irreg med pbles	(35)						(5)	(0)				(57)	Phos(3) & lge fel spar grains. Intergstial ?apatite	17,8	1,40	12,71
	Matrix	25	M	S	P	V	0	<5	0	-	-	0	C,GlNI	type phos with phosized edges			
	Pebbles	<1	S	S	?	0	0	<5	?15	P	0	0	M,C				
A5407B	Yel gry to olv gry rnded lge cobbles smooth surf with enclosed NI phos pbles.													Phos grains present	15,9	2,59	6,13
	Matrix	25	L	S,P	P	V	M	<5	<1	P	0	0	C				
	Pebbles	<1	M	?P	0	0	0	10	<5	P	0	0	M,C	Iron-rich matrix			
														AVERAGE	18,3	1,92	9,99
(b) Saldanha Bay Region																	
2219E	Lt olv gry irreg crse pbles smooth surf.																
	Matrix	30	M,L	S,P	V	V	0	1	0	-	-	0	C	Sim to cmt but more gl & qz	22,2	1,64	13,53
	Pebbles	<5	S,M	S,P	V	V	0	1	15	P	0	0	M				
2219F(ii)	Gryish olv crse pbles gritty surf																
	Matrix	>50	L	S,P	P	V	0	<5	<5	P	0	0	C,M	Phos grains common	14,3	4,06	3,52
	Pebbles	10	S	S	V	0	0	15	5	P	0	0	M,C				
2230C	Sim to 2220(F) but encl pbles smaller													V sim to 2219F(ii)			
	Matrix	30	L	S,P	P	V	0	<5	<1	P	0	0	C,M	Phos grains common	17,1	2,88	5,93
	Pebbles	1	S	S	V	0	0	15	5	P	V	0	M,C				

CI CLASS PHOSPHORITES (Continued)

SAMPLE NUMBER	HAND SPECIMEN DESCRIPTION	PETROGRAPHIC ANALYSIS													CHEMISTRY		
		GLAUCONITE							FORAMS								
		%	size	shape	mottl	rims	oxid	% quartz	%	plank benth	filled	macrofos	cement	COMMENTS	P_2O_5	K_2O	P_2O_5/K_2O
2231	Variable in colour yel gry to olv gry irreg small cobbles smooth surf.Large encl. pbles.																
	Matrix	15	S,M	S	V	V	O	<5	O	-	-	O	C	Pbles partially gl ized	22,4	1,35	16,59
	Pebbles	<1	S	S	O	O	O	<1	30	P	V	O	C,M				
2240A(i)& (ii)	Pl yel brn to gryish olv irreg ovoid lge cobbles with bone(i) & without bone(ii) encl.	(38)						(2)	(3)			(54)		Pbles partially gl ized			
	Matrix	30	M,L	S,P	V	V	O	<5	1	P	O	O	C,M	Phos grains present(2) (i)	23,4	0,74	31,62
	Pebbles	<1	S	S	V	O	O	<5	10	P	M	O	M	Phos filled foramS (ii)	18,8	2,18	8,62
	Pebbles	30	M,L	S,P	V	V	O	<5	1	P	O	O	C,M	Pbles same as cement			
2241	Dsky yel to gryish olv irreg ovoid small cobbles with smooth surf.													V sim to 2240. Phos grains present	ts	ts	ts
	Matrix	30	M,L	S,P	P	O	O	<5	<1	P	O	O	C				
	Pebbles	O	-	-	-	-	-	<1	15	P	V	O	M				
2247A	Gryish yel grn angular crse pebbles													*Interstial? apatite&phos grains present V sim to 2240 less & smaller gl			
	Matrix	25	S,P	S	M*	M	M	<5	<1	P	?	O	C,G		,17,8	1,05	16,95
	Pebbles	O	-	-	-	-	-	<1	15	P	V	O	M				
2786	Yelish gry to gryish grn v irreg lge cobbles	(28)						(5)	(0)			(66)		Felspar present			
	Matrix	25	S,L	S,P	V	M	O	<5	O	-	-	O	C,M	Pble margins not distinct	19,4	1,44	12,47
	Pebbles	<1	S,M	S	V	O	O	5	10	P	O	O	M				
														AVERAGE	19,4	1,92	13,78

CI CLASS PHOSPHORITES (Continued)

SAMPLE NUMBER	HAND SPECIMEN DESCRIPTION	PETROGRAPHIC ANALYSIS													CHEMISTRY		
		GLAUCONITE						% quartz	FORAMS			macrofos	cement	COMMENTS	P_2O_5	K_2O	P_2O_5/K_2O
		%	size	shape	mottl	rims	oxid		%	plank benth	filled						
(c) Childs Bank Region																	
	None																
														AVERAGE FOR CI PHOSPHORITES	18,9	1,92	12,1
CII CLASS PHOSPHORITES																	
(a) Cape Peninsula Region																	
	None																
(b) Saldanha Bay Region																	
	None																
(c) Childs Bank Region																	
2462 (dredge)	Dk yel brown irreg crse pbles with smooth surf													Interstial?apatite) Phos or goethite)			
	Matrix	<1	S	S	P	V	0	<1	<5	P,B	0	P	C?Go	in fillings & frag)	22,2	0,89	24,94
	Pebbles	0	-	-	-	-	-	0	5	P	0	0	M	v common)			
2486	Dk yel oran to yelish gry tabloid cobbles with v angular surf.													Sim to 2841B Cora-) line algae pres v)			
	Matrix	0	-	-	-	-	-	0	<1	P,B	0	P	G1,C,Go	complex compositi-)	26,5	0,32	82,81
	Pebbles	0	-	-	-	-	-	0	5	P	0	0	C,Go	on.Mostly unident) shell debris)			
2487B	Dsky oran lge cobbles-size slabs with one pitted surf & other with lge bored cavities Approx.total rk composn 500 cts													Intertial?apatite) Not strictly a CII)			
	Matrix	0	-	-	-	-	-	<1	15	P,B	0	0	G1,C,Go	phos,no macrofossils)			
		(0)						(0)	(5)		(1)	(0)		Clear fibrous rims)	25,8	0,32	80,62
	Pebbles	0	-	-	-	-	-	<1	10	P	0	0	M,Go *	(?apatite)around) some carbonate) grains. Bone pres.) *dk brn micrite 55;			

SAMPLE NUMBER	HAND SPECIMEN DESCRIPTION	PETROGRAPHIC ANALYSIS													CHEMISTRY		
		GLAUCONITE							FORAMS					COMMENTS			
		%	size	shape	mottl	rims	oxid	% quartz	%	plank benth	filled	macrofos	cement		P_2O_5	K_2O	P_2O_5/K_2O
2487B (continued)														?collo(dk brn in cross nichols & in plain polarizd light) 31;gl matrix 5; foram infillings 1; unident.8.			
														AVERAGE	24,8	0,51	62,79
MISCELLANEOUS PHOSPHORITES TYPES																	
(a) Cape Peninsula Region																	
1692C NII/NIIIA	Dk yel brn (NII areas) to lt olv gry large cobble slabs.	(0)							(6)	(5)				(74)Bryozoa common(6) Unident(9)			
		NII	<1	M	S	P	0	0	<5	5	B,P	0	0	Go			
			(8)							(11)	(3)			(67)Forams filled with	16,5	0,73	22,60
		NIIIA	5	P	S	V	0	0	5	5	P,B	0	0	CGo Gl/?Go(6)			
(b) Saldanha Bay Region																	
2219F(1) NIIIA/ NIIIA	Gryish olv crse pbles gritty surf secondary layering													Matrix lt brn & shows parll sut- urg			
		NIIIA	40	L,M	S	P	M	0	<1	5	P	0	0	M,C	14,3	4,06	3,52
														Matrix dk brn &			
		NIIIA	15	L	S	P	M	0	<1	<1	P	0	0	C,M shows parll suturg)			
2266B NI/NIIIA	Lt yel gry ovoid small cobbles smooth surf with secondry layerg.													Matrix & forams glized,foram ghosts remain			
		NIA	0	-	-	-	-	-	1	0	-	-	0	Gl	22,2	1,26	17,61
		NIIIA	>50	L	S,P	P	V	0	<1	0	P	0	0	C,M Phos grains common)			

MISCELLANEOUS PHOSPHORITES TYPES (Continued)

SAMPLE NUMBER	HAND SPECIMEN DESCRIPTION		PETROGRAPHIC ANALYSIS													CHEMISTRY		
			GLAUCONITE						% quartz	FORAMS			macrofos	cement	COMMENTS	P_2O_5	K_2O	P_2O_5/K_2O
			%	size	shape	mottl	rims	oxid		%	plank benth	filled						
2254C CII/NIA	Pl yelish oran to med yel brn irreg large cobbles one v bored surf	Matrix	<5	S,M	S	P	O	O	<5	<5	B,P	M	P	C,Go	Large pecten sp. abundant			
		Pebbles	10	S	S	V	M	O	15	0	-	-	P	C	Iron-rich matrix			
		Pebbles	<1	S	S	P	O	O	<1	5	B,P	M	V	Go	Iron-rich NII pbls V variable composn	13,9	1,09	12,75
		NIA	<1	S	S	P	O	O	<1	30	P,B	V	O	M,Go	Frags of CII pres.			
	Approx. total rk composition, 500 cts.		(3)						(6)	(2)		*	*		*Collo 61;?Go/Gl fillings 3;go cement 23; unident.carbonates 2			
(c) Childs Bank Region																		
2361D CI/NII	Mod yel brn to olv gry ovoid large cobbles with smooth surf & large cavities	Matrix	20	M	S	V	V	O	<5	0	-	-	O	C				
		Pebbles	0	-	-	-	-	-	0	25	P,B	P	O	Go	Most forams filled Typical NII phos	22,0	1,04	60,40
		Pebbles	0	-	-	-	-	-	0	0	-	-	O	Go,C	Contains Nummulites sp.			
2449A CI/CII	Yelish brn (ferruginous parts) to dk gry irreg-tabloid large smooth surf	Matrix	15	M	S	P	V	P	<1	0	-	-	M	C,Go	Gl Iron assoct(withg)			
		Pebbles	0	-	-	-	-	-	0	30	P,B	M	O	C,Go	Also bone bryozoa & NII frags	26,8	0,68	39,41
		Matrix	0	-	-	-	-	-	0	0	-	-	V	Go				
		Pebbles	0	-	-	-	-	-	0	20	P,B	V	O	Go	Also bone & macrofossils.Difficult to classify			
	Approx total rk composition, 300 cts		(5)						(0,3)	(8)		*	*		*Micrite/?microspar 57;go/gl infillings 14;unident carbonate frags 16			

MISCELLANEOUS PHOSPHORITES TYPES (Continued)

SAMPLE NUMBER	HAND SPECIMEN DESCRIPTION		PETROGRAPHIC ANALYSIS													CHEMISTRY		
			GLAUCONITE						% quartz	FORAMS			macrofos	cement	COMMENTS	P_2O_5	K_2O	P_2O_5/K_2O
			%	size	shape	mottl	rims	oxid		%	plank benth	filled						
2460 NIIIA/ CII	Dsky yel to lt olv gry v large cobble slabs extremely knobby surf with abundant macrofossils		(20)						(2)	(0)			(0)	(03)	Distinctive NII frags & Go infills)			
		NIIIA	15	S,M	S	P	V	P	<1	0	-	-	0	C,M	(15)derivd from CII part of the rk)			
		CII (Matrix	0	-	-	-	-	-	0	40	P,B	V	V	C,Go	Cmt only partially goethite	18,8	0,53	37,35
		CII (Pebbles	0	-	-	-	-	-	0	40	P,B	P	0		Also macrofossiliferous pbles			
2483A&B NI/GPL	Yelish gry lge cobble-size slabs with lge borings & cavities. Some show internal layerg & is sometimes coated with GPL														This NI phos exhib its both phosized & gl ized edges. Secondary GPL coating on one surf			
		NI	0	-	-	-	-	-	0	50	P	0	0	M,C,Gl				
		GPL	1	S	S	P	0	0	<1	20	P	0	0	M,C		17,4	0,56	31,07
															AVERAGE FOR THIS GROUP	19,8	0,84	31,59

IV - B. Wholerock and micro-analysis of phosphatic and glauconitic materials - methods and results

(i) Methods.

Whole rock chemical analyses.

Samples were prepared on the lines set out by Parker (1971), but the presence of fluorine in the phosphorites requires special treatment for loss of fusion determinations. When the sample is heated fluorine in the francolite mineral is liberated and combines with structurally bonded water to form HF, a toxic gas which attacks silica crucibles. It is therefore necessary to use only platinum dishes and to pre-heat the phosphorite powder over a bunsen burner at 950°C for ½ hour in a fume cupboard to liberate most of the volatiles before placing in an oven at 1000°C for 12 hours.

Chemical analyses were conducted in the Department of Geochemistry, UCT, by X-ray fluorescence procedures using a PW 1220 semi-automatic spectrometer and methods described by Willis et al. (1971). Si, Al, Ti, Ca, K, Mg, Mn, Fe and P were determined on fusion discs prepared after the method of Norrish and Hutton (1969) and Na was determined on 4 grams of powder ground to -300 mesh and pressed into briquettes. The method was calibrated by analysing departmental and international standards at frequent intervals during the determinations (Table AIV-1).

Raw data was processed using computer programmes written in the Department which calculate working curves from the standards and make necessary corrections for spectral line interference, dead time and matrix effects. Analytical conditions for the major element determinations are set out below. A conglomeratic phosphorite (Dr-4) analysed by Parker (1971) was resampled and included in this study to act as an additional check on subsampling, sample preparation as well as analytical techniques. The composition of the rock as determined by Parker (1971) and in this work, is also presented for comparison.

Analytical conditions:

Element	Tube	KV	mA	Counter	Collimotor	Crystal
Ti	Cr	50	20	flow	coarse	Lif
Ca	Cr	50	20	flow	fine	Lif
K	Cr	50	20	flow	coarse	Lif
Si	Cr	50	32	flow	coarse	Pet
Al	Cr	50	32	flow	coarse	Pet
Mg	Cr	50	32	flow	coarse	ADP
P	Cr	50	32	flow	coarse	Germanium
Na	Cr	50	32	flow	coarse	Gypsum
Fe	Au	50	20	flow	fine	Lif
Mn	Au	50	20	flow	fine	Lif

Table AIV-1. Adopted values for X-ray flourescence standards.

Standard	SiO_2	TiO_2	Al_2O_3	Fe_2O_3 (1)	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5
GH	75,79		12,62		0,05				4,78	
AGV-1	59,08	1,05	17,06	6,79	0,10					0,49
S-1	59,58			8,30	0,40		10,10			
BCR-1	54,50	2,20	13,61	13,40	0,18		6,92		1,70	0,36
NIM-1	51,15					25,25				
PCC-1	41,88			8,23	0,12	43,22				
GSP-1	67,38	0,66	15,25	4,33	0,04				5,53	0,28
W-1	52,60	1,08	14,90	11,12	0,17	6,62	10,92	2,15	0,64	0,14
OK-272			16,34					5,25		
DTS-1				8,64		49,80				
PDC-1 (2)							14,83			10,17
PDC-2 (2)							22,52			15,45
PDC-3 (2)							30,40			20,84
PDC-4 (2)							46,60			31,95
PDC-5 (2)							50,70			34,70
KL-11						6,69	10,97			
PG-11						0,28				
MRG-1								0,62		

(1) Total Fe

(2) Standards supplied by Phosphate Development Corporation.

Phosphorite Dr-4 (310)

	Parker, 1971	This work
SiO_2	24,89	23,78
TiO_2	0,20	0,15
Al_2O_3	3,18	2,64
Fe_2O_3(1)	4,32	6,49
MnO	0,01	0,01
MgO	1,19	1,88
CaO	31,81	30,98
Na_2O	0,95	0,64
K_2O	1,70	2,63
P_2O_5	18,79	18,74
F	2,05	2,56
S	0,58	-
LOF	11,04	10,47
total	100,71	100,97

(1) total iron as Fe_2O_3

Fluorine analyses

Fluorine determinations were made by the Phosphate Development Corporation using a fluoride specific ion electrode technique. An Orion Research Ionalyzer Model 801/Digital instrument was calibrated against sodium fluoride.

Analyses were run singleton except for an onland sample (Site 6) which was determined six times in order to estimate the precision of the instrument. Although the precision was reasonable (3,17%), the method has been found to give distinctly low values (Parker, 1971). However F values for sample Dr-4 as determined in this work were higher than those analysed by Parker by approximately the same amount as his were low. Therefore no adjustment has been made to the fluorine results reported here.

Replicate analyses of sample from Site 6

	1,98
	1,95
	1,75
	1,89
	1,88
	1,87
$\bar{x}$	1,89
Sx	0,06
Rel.Dev.	3,17

Organic carbon determinations.

The same technique was used on the phosphorite rocks as for the unconsolidated sediment.

Microprobe analytical procedures.

Glauconite grains were mounted in araldite, thin-sectioned and double-polished before mounting on graduated slides for easy grain identification.

Minerals were analysed for Si, Al, Fe, Mg, Ca, Na, K, P and sometimes S with a Cambridge Microscan V microprobe in the Department of Geochemistry, University of Cape Town under the guidance of Messrs. J.P. Willis and R. Richard. The raw data was corrected and reduced using ABFAN, a computer programme written by Boyd, Finger and Chayes (1968)(Ann.Rept.Div.Geophys.Lab., Washington, 1967-1968, 210-215). Kα lines for the 9 elements were measured at 15 Kv with a total beam current of 0.5×10^{-6} amps. The following analyzing crystals were used: RAP crystal for Si, Al, Mg and Na; Quartz for Fe, Ca and K; and PET for P and S.

To prevent the volatilisation of Na and K from the sample area under the electron beam, it was necessary, in addition to reducing the beam current from the usual 1.5 to 0.5 micro-amps, to use a defocused beam. Experiments showed that no loss of intensity occurred as long as the spot diameter was less than 30μm. Spot diameters between 10 & 20μm were used in this work, and no measurable loss of alkali elements was noticed in the counting times employed (20 seconds).

B(ii) Results of whole rock analyses of onland and off-shore phosphorites

SAMPLE NO.	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	Na_2O	P_2O_5	MnO	L.O.F.	TOTAL	F	CaO/P_2O_5	Corg	F/P_2O_5	Al_2O_3/K_2O
(a) Offshore phosphorites																	
1706 NI	13,06	0,12	1,94	1,52	1,15	42,77	0,61	1,01	14,26	0,02	23,25	99,71	1,96	3,00	0,44	0,14	3,18
2219 NI	1,63	0,13	1,63	1,98	1,03	45,53	0,83	1,13	21,74	0,01	15,43	89,04	3,00	2,00	0,77	0,14	2,04
2703 NI	1,63	0,03	0,45	0,81	1,01	50,45	0,21	1,28	20,87	0,01	22,59	99,34	2,80	2,42	0,51	0,14	2,14
2461 NI	1,34	0,03	0,47	2,43	0,97	50,56	0,15	0,94	18,17	0,02	24,68	99,76	2,53	2,78	0,36	0,14	3,13
1692 NII	12,06	0,12	2,05	11,11	1,17	37,67	0,57	0,96	15,42	0,04	19,02	100,19	2,10	2,44	0,31	0,14	3,60
1700 NIII	21,56	0,14	2,62	5,15	1,68	34,16	2,13	1,01	19,95	0,01	12,73	101,14	2,77	1,71	0,64	0,14	1,23
2220 NIII	29,38	0,13	2,01	2,52	0,84	32,82	1,61	1,00	15,91	0,01	13,68	99,91	2,15	2,06	0,50	0,14	2,23
2254 NIII	24,50	0,08	2,51	10,08	2,34	27,35	3,64	0,87	16,84	0,01	10,88	99,10	2,15	1,62	0,43	0,13	0,69
DR-4 NIII	23,78	0,15	2,64	6,49	1,88	30,98	2,63	0,64	18,74	0,01	10,47	98,41	2,56	1,65	0,58	0,14	1,00
1706 CI	20,59	0,14	2,02	3,96	1,23	34,34	1,66	1,19	17,88	0,01	16,65	99,67	2,42	1,92	0,62	0,14	1,22
2240 CI	18,46	0,08	2,01	6,92	1,82	32,96	2,67	1,18	19,42	0,01	12,44	97,97	2,60	1,70	0,50	0,14	0,75
2786 CI	20,22	0,12	1,65	4,64	1,32	34,63	1,70	1,18	19,47	0,01	13,13	98,07	2,61	1,78	0,81	0,14	0,97
2254 CII	13,94	0,13	1,47	5,24	1,72	40,82	0,91	0,67	15,41	0,05	20,48	100,84	2,22	2,65	0,11	0,14	1,62
2449 Misc	5,37	0,06	0,98	4,50	0,22	45,09	0,78	1,03	20,89	0,03	19,76	98,71	2,85	2,16	0,47	0,14	1,26
2460 Misc	5,90	0,09	1,43	3,52	1,07	44,87	0,62	1,19	20,36	0,01	20,59	99,65	2,77	2,20	0,45	0,14	2,31
(b) Onland phosphorites																	
SITE-IA	56,89	0,66	5,65	3,01	0,10	13,55	0,23	0,45	13,53	0,02	5,30	99,39	1,05	1,00	0,15	0,08	24,57
SITE-3-GRDN	70,76	0,08	8,38	4,87	0,10	1,57	0,26	0,13	5,78	0,02	6,65	98,60	0,12	0,27	0,20	0,02	32,23
SITE-5-SKSG	58,18	0,09	2,09	0,81	0,18	19,94	0,50	0,09	14,38	0,003	5,20	101,46	1,41	1,39	0,23	0,10	4,18
SITE-7-VWB	45,60	0,15	1,44	0,88	0,26	25,98	0,49	0,19	18,32	0,004	6,15	99,46	1,65	1,42	0,37	0,09	2,94
SITE-7-VWF	54,69	0,13	1,05	0,25	0,14	22,81	0,07	0,17	16,57	0,001	5,68	101,56	1,95	1,38	0,18	0,12	15,00
SITE-6 B	4,12	0,04	1,51	0,37	0,69	47,46	0,20	1,02	33,82	0,03	9,82	99,08	1,66	1,40	0,33	0,05	7,55
SITE 9	47,70	0,04	1,13	3,02	0,21	25,38	0,02	0,10	18,36	0,003	6,07	102,03	1,70	1,38	0,44	0,09	56,50

B(iii) Location and description of materials analysed using the electron microprobe.

Analysis number	Station number	Position on slide	Description of material analysed
1	2834.G	U/14	Dark green, rounded, sutured glauconite grain.
2	2834.G	W/16	Green, more glauconitic centre of mottled phospho-glauconite grain.
3	2834.G	W/16	Yellow-green, phosphate-rich core of above grain.
4	2247.G	P/15	Dark green, sutured glauconite grain.
5	2247.G	Q/9	Dark green, sutured, well rounded, glauconite grain.
6	2247.G	T,U/11	Dark green, sutured, glauconite grain.
7	2247.G	T,U/11	Dark green, sutured, glauconite grain.
8	2247.G	O/13,14	Dark green, sutured, glauconite grain.
9	1706.G	-U/6	Uniform lime-green, glauco-phosphatic infilling.
10	1706.G	±U/6	Homogeneous dark green, well rounded glauconite grain.
12	1706.G	±S/7,8	Dark green, rounded glauconite grain.
13	1706.G	±T,U/6,7	Dark green, rounded, sutured glauconite grain.
14	1706.G	S/11	Dark green, rounded, sutured glauconite grain.
15	1706.G	R/12	Dark green, glauconite with small Ca-rich inclusions.
16	2716.G	-	Uniform dark green, sutured glauconite grain.
17	2716.G	O/4	Uniform dark green, sutured glauconite.
18	3111.G	±T/10	Uniform dark green, sutured glauconite grain.
19	3111.G	±N/14	Uniform dark green, sutured glauconite grain.
20	3111.G	±N/14	Dark green non-sutured glauconite grain.
21	3111.G	±Q/11	Dark green sutured glauconite grain.
22	3111.G	Q/7	Dark green sutured glauconite grain.
23	3111.G	R,S/17	Yellow, phosphate-rich rim of dark green phosphatized glauconite.
24	2465.G	R,S/17	Central glauconitic portion of above grain.
25	2465.G	U/14	Yellow, phosphatic region of mottled dark green glauconite.
26	2465.G	U/14	Dark green, glauconite-rich portion of above grain.
27	1698.G	N/7	Slightly phosphatic dark green glauconite.
28	1698.G	L/9	Slightly phosphatic, light green, sutured glauconite.
29	1698.G	M/20	Slightly phosphatic, glauconite grain.
30	1698.G	M/19	Slightly yellow-green, very sutured subrounded glauconite grain.
31	1698.G	S/14	Phosphatic glauconite grain.
32	2834.G	S/8	Finely mottled phospho-glauconite.
33	2834.G	J/18	Uniformly yellow-green glauco-phosphate grain.
34	2465.G	J/17	Extremely heterogenous yellow-green phospho-glauconite grain.
35	2465.G	G/7	Zoned phospho-glauconite grain.
36	2834.G	N/5	Coarse mottled phospho-glauconite grain.
37	2834.G	L/6	Coarse mottled phospho-glauconite grain.
38	2834.G	T/14	Coarse mottled phospho-glauconite grain.
39	1698.G	O/11	Phosphatic yellow-green, very sutured glauconite.
40	1698.G	N/17	Slightly phosphatic yellowish-orange green glauconite
41	1698.G	O/20	Slightly phosphatic lime-green irregular-shaped glauconite.
42	1698.G	O/9	Slightly phosphatic brown, irregular non-sutured immature glauconite.
43	1698.G	U,V/19,20	Uniform, dark green sutured glauconite.
44	1698.G	P/6	Uniform, green well rounded glauconite grain.

Analysis number	Station number	Position on slide	Description of material analysed
45	1698.G	U,V/19	Lime-green, slightly sutured irregular glauconite grain.
46	1698.G	L,M/16	Slightly phosphatic brown grain with quartz inclusions.
47	1698.G	L,M/16	Very dark brown (?) oxidized glauconite.
48	1698.G	P/17	Uniform dark green non-sutured glauconite.
49	1698.G	R/7,8	Dark green, well rounded glauconite.
50	1698.G	U,T/16,17	Very sutured medium green glauconite pellet.
51	1698.G	K/16,17	Dark green, slightly sutured glauconite.
52	2834.G	Q/21	Uniform lime green, slightly phosphatic grain with inclusions.
53	2834.G	G,H/17,18	Very slightly phosphatic, lime-green grain with quartz inclusions.
54	2834.G	H,J/11	Phosphatic dark green glauconite grain.
55	2834.G	C,D/10	Slightly phosphatic uniform lime-green sutured grain with quartz inclusions.
56	2834.G	T/6	Lime-green, non-sutured very immature glauconite.
57	2834.G	Q/10	Dark brown, heterogeneous, non-sutured very immature glauconite.
58	2834.G	Q/10	Heterogeneous, dark brown, non-sutured very immature glauconite.
59	3111.G	W/9	Lime-green foram. infilling.
60	3111.G	O/10	Uniform, sutured, medium green glauconite.
61	3111.G	O/10	Slightly phosphatic, medium green, homogeneous, foram infilling.
62	3111.G	R/10	Dark brown foram. infilling.
63	3111.G	S/10	Dark lime-green, non-sutured grain with inclusions and dark (?) organic-rich areas.
65	3111.G	U/11	Lime-green glauconite, non-sutured, no inclusions with darker (?) organic-rich regions.
71	3111.G	U/10	Lime-green foram. infilling.
73	2710.G	-	Green, very zoned glauconite.
74	310.D	-	Lime-green phosphatic foram. infilling in matrix of similar composition.
75	310.D	-	Light-greenish brown glauco-phosphatic matrix.
76	310.D	-	Light-greenish brown glauco-phosphatic matrix.
77	310.D	-	Light-greenish brown, glauco-phosphatic matrix.
78	310.D	-	Light brown phosphorite matrix.
79	310.D	-	Light brown phosphorite matrix.
80	310.D	-	Light brown phosphorite matrix.
81	310.D	-	Light brown phosphorite matrix.
82	310.D	-	Light brown phosphorite matrix.
83	-	U/14,15	Calcium-rich portion of immature glauconite grain.
84	-	U/14,15	Calcium-rich portion of immature glauconite grain.
85	-	T,U/14	Calcium-rich portion of grain below.
86	-	T,U/14	Yellowish-green, non-sutured immature glauconite.
96	-	-	Glauco-phosphatic faecal pellet.
97	-	-	Glauco-phosphatic faecal pellet.
98	-	-	Glauconitized faecal pellet.
99	-	-	Phosphatized faecal pellet.
100	-	-	Phosphatized faecal pellet.
101	-	-	Phosphatized faecal pellet.
102	-	-	Phosphatized faecal pellet.
103	2246.D	$B^1/1$	Dark brown phosphate matrix, 1st analysis.
104	2246.D	$B^1/1$	Dark brown phosphate matrix, 2nd analysis.

Analysis number	Station number	Position on slide	Description of material analysed
105	2266.D	M/3	Lime-green foram. infilling.
106	2266.D	T/7	Medium lime-green foram. infilling.
107	2266.D	T/7	Lime-green glauco-phosphate grain.
108	2266.D	Z,A^1/16,17	Orange, slightly lime-green glauco-phosphate matrix.
109	2266.D	Z,A^1/16	Lime-green glauco-phosphate grain. 1st analysis.
110	2266.D	Z,A^1/16	Lime-green, glauco-phosphate grain. 2nd analysis.
111	2495.D	V,W/12	Orange, iron-rich foram. infilling.
112	2495.D	R/11	Colourless phosphate ambient matrix.
113	2495.D	R/11	Orange, iron-rich foram. infilling.
114	2495.D	Q/12	Colourless, glauco-phosphatic ambient matrix. 1st analysis.
115	2495.D	Q/12	Colourless, glauco-phosphatic ambient matrix. 2nd analysis.
116	2495.D	Q/12	Orange, iron-rich foram. infilling. 1st analysis.
117	2495.D	Q/12	Orange, iron-rich foram. infilling. 2nd analysis.
118	310.D	W/14	Dark brown phosphate matrix.
119	310.D	W/14	Dark brown, phosphate matrix.
120	310.D	W/14	Brownish-green to lime-green glauco-phosphatic matrix.
121	310.D	W/14	Lime-green glauco-phosphate grain in matrix of similar composition.
122	310.D	W/14	Dark green mottled glauconite in glauco-phosphate matrix.
123	310.D	X,Z/4,5	Dark brown mottled glauconite in glauco-phosphate matrix. 2nd analysis.
124	310D	X,Z/4,5	Dark brown (?) organic-rich glauco-phosphate matrix. 1st analysis.
125	310.D	W,Y/4,5	Phosphate inclusion in matrix. 1st analysis.
126	310.D	W,Y/4,5	Phosphate inclusion in matrix. 2nd analysis.
127	2825.G	-	Phosphatized faecal pellet.
128	2825.G	-	Phosphatized faecal pellet.
129	2825.G	-	Phosphatized faecal pellet with speckles and dark outer rim.
130	2825.G	-	Phosphatized faecal pellet.
131	2266.D	-	Post-depositional lime-green phospho-glauconite intrusive vein.
132	2266.D	-	Post-depositional lime-green phospho-glauconite intrusive vein.
133	2266.D	-	Post-depositional glauco-phosphatic matrix, some intrusion.
134	2266.D	-	Post-depositional phospho-glauconite matrix. 2nd intrusive vein.
135	2266.D	-	Post-depositional phospho-glauconite matrix. 2nd intrusive vein.
136	2266.D	-	Very light orange foram. infilling.
137	2266.D	-	Light brown matrix.
138	2486.D	-	Post-depositional lime-green phospho-glauconite intrusive vein.
139	2486.D	-	Post-depositional brown phosphate intrusive vein.
140	2486.D	-	Post-depositional lime-green phospho-glauconite intrusive vein.
142	GIL-574.D	W/16,17	Central un-oxidized portion of oxidized glauconite grain.
143	GIL 574.D	W/16,17	Oxidized rim of oxidized glauconite grain.
144	GIL 574.D	S/7	Central unoxidized portion of oxidized glauconite grain.

Analysis number	Station number	Position on slide	Description of material analysed
145	GIL-574.D	S/7	Oxidized rim of oxidized glauconite grain.
146	GIL-574.D	V/13	Very dark green oxidized, iron-rich glauconite grain.
147	GIL-574.D	V/7	Very large golden brown, extremely iron-rich oxidized glauconite grain.
148	GIL-574.D	U/6	Dark green unoxidized glauconite grain from same slide.
149	GIL-574.D	U/6	Ambient phosphate matrix.
150	2834.G	V/16	Phosphate-rich portion of coarsely mottled glauco-phosphate grain.
152	2834.G	R/18	Glauconitic core of phosphatized glauconite grain.
153	2834.G	R/18	Phosphatic rim of phosphatized glauconite grain.
154	2834.G	R/18	Analysis between the glauconitic core and the phosphatic rim.
155	2834.G	J/18	More glauconitic central portion of finely mottled glauco-phosphate grain.
156	2834.G	J/18	Phosphate-rich rim of finely mottled glauco-phosphate grain.
157	2465.G	X/13	Brown phosphate foram. infilling.
158	2465.G	J/17	Heterogenous glauco-phosphate grain.
159	2465.G	G/7	Phosphatic core of glauconite grain.
160	2465.G	G/7	Glauconite-rich rim of above grain.
161	2688.G	F/7	More glauconitic outer test of infilled foram.
162	2688.G	F/7	Outer more phosphate-rich material of foram. infilling.
163	2688.G	V/16	Inner glauconitic test of infilled foram.
165	S.F.	-	Ambient colourless matrix.
166	S.F. S.F.	-	Phosphatized (? faecal pellet) inclusion in above matrix.
167	S.F.	-	Phosphatized (? faecal pellet) inclusion. 2nd analysis.
168	S.F.	-	Ambient colourless matrix.
169	S.F.	-	Phosphatized inclusion with bone nucleus.
170	S.F.	-	Second analysis of above grain.
172	S.F.	J/20	Dark brown phosphatic inclusion.
173	S.F.	J/20	Dark brown phosphatic inclusion.
176	S.F.	L/18	Colourless ambient phosphatic matrix.
181	S.F.	D/16	Dark brown phosphatic pellet inclusion.
182	3346	V/6	Ovoid pelletal phosphorite grain from medium sand-size fraction.
183	3346	V/6	Centre of above grain.
184	3346	V/6	Rim of above grain.
185	3346	V/6	Centre of ovoid pelletal phosphorite grain.
186	3346	V,W/8	Centre of ovoid pelletal phosphorite grain.
187	3346	V,W/8	Rim of above grain.
188	3346	K/16	Centre of pelletal phosphorite grain.
189	3346	K/16	Rim of above grain.
190	3346	L/16	Homogeneous pelletal phosphorite grain.
191	3346	V/5	Heterogeneous pelletal phosphorite grain.
192	3346	V/5	Second analysis of above grain.
193	3346	V/6	Sutured phospho-glauconite grain.
194	3346	V/7	Homogeneous pelletal phosphorite grain.

Analysis number	Station number	Position on slide	Description of material analysed
195	SKSIG	D/9	Light brown matrix of Skoongesig phosphatic sandstone.
196	SKSIG	D/9	Large dark orange inclusion in above matrix.
198	SKSIG	D/8	Second analysis of light brown matrix.
200	SKSIG	D/8	Second analysis of large dark orange inclusion.
201	SKSIG	D/8	Third analysis of dark orange inclusion.
204	S.F.	U/16	Dark brown phosphatic inclusion in Varswater Formation.
205	S.F.	U/16	Light brown ambient matrix.
206	S.F.	U/17	Second analysis of light brown ambient matrix.
207	S.F.	U/16	Second analysis of dark brown inclusion.

S.F. - Varswater and Saldanha Formation.
SKSIG - Skoongesig phosphorite

B(iv) Results of microprobe analyses of offshore phosphorite and glauconite

(a) GLAUCONITE PELLETS

First Stage Glauconites

Analysis Number	K_2O	Na_2O	Fe_2O_3	SiO_2	CaO	Al_2O_3	P_2O_5	MgO
42	5,45	,14	18,61	48,81	,50	6,32	,19	4,32
46	5,28	,17	17,55	50,69	,89	7,39	,41	4,38
53	5,40	,15	20,09	48,75	2,04	5,29	,19	3,95
56	4,64	,08	19,01	43,22	3,51	4,14	,13	3,55
58	5,02	,15	20,83	48,35	2,71	4,06	,14	3,73
63	5,55	,14	18,76	48,33	,40	7,21	,05	4,33
Means	5,22	,14	19,14	48,03	1,68	5,74	,19	4,04

Second Stage Glauconites

28	6,26	,11	19,19	50,97	,94	4,29	,55	3,99
29	6,51	,11	22,38	50,37	,37	4,07	,16	4,48
30	6,15	,06	20,17	51,88	,19	5,00	,06	4,48
40	7,03	,26	22,01	48,55	,19	4,59	,16	4,29
41	6,70	,12	23,59	46,92	,23	4,27	,14	3,73
45	6,40	,13	20,79	51,07	,24	5,09	,14	4,44
47	6,96	,10	23,55	48,63	,20	5,46	,27	4,20
52	6,82	,03	20,35	50,90	,69	5,65	,38	4,56
55	6,72	,08	19,24	50,54	,36	5,10	,16	5,00
73	7,09	,49	23,57	44,74	,09	1,97	,14	4,22
142	6,75	,57	27,07	48,13	,14	3,60	,14	3,83
148	7,35	,30	27,27	50,00	,18	2,55	,08	3,75
Means	6,73	,19	22,43	49,39	,32	4,30	,20	4,25

Third Stage Glauconites

24	8,13	,06	21,27	50,12	,23	5,35	,40	4,53
27	8,41	,10	25,07	18,01	,24	3,09	,22	4,23
43	8,05	,05	21,76	49,79	,21	5,06	,08	4,32
44	7,73	,10	19,60	50,56	,16	5,50	,05	4,43
48	8,08	,08	23,07	51,66	,17	3,81	,08	4,32
49	7,81	,05	22,92	51,74	,26	2,94	,05	4,41
50	7,92	,11	20,73	51,81	,24	5,13	,05	4,39
51	7,74	,10	22,15	51,71	,26	3,72	,03	4,34
193	7,75	,03	20,21	51,91	01,13	06,47	00,58	05,15
Means	7,96	,08	21,86	50,81	,32	4,56	,17	4,46

Fourth Stage Glauconites

Analysis Number	K_2O	Na_2O	Fe_2O_3	SiO_2	CaO	Al_2O_3	P_2O_5	MgO
1	8,79	,10	21,64	51,06	,14	3,74	,05	5,67
4	8,79	,15	22,37	50,58	,14	3,98	,07	4,65
5	9,17	,07	22,46	52,06	,08	2,21	,05	5,57
6	9,32	,06	21,58	51,51	,11	3,49	,05	5,27
7	8,55	,02	20,93	51,63	,17	4,74	,07	4,72
8	8,76	,07	23,76	51,62	,18	1,97	,05	5,05
10	8,85	,05	21,85	49,94	,81	4,03	,12	5,39
12	8,79	,05	21,98	50,86	,16	5,08	,07	5,10
13	8,99	,06	21,77	51,38	,17	4,21	,07	5,61
14	9,05	,10	21,53	50,56	,12	4,23	,09	5,58
15	8,70	,08	23,54	50,23	,18	2,07	,07	5,79
16	9,47	,02	18,88	50,82	,04	4,20	,08	5,54
17	9,41	,05	17,72	51,27	,14	5,31	,41	5,79
18	9,21	,07	22,85	51,04	,11	2,46	,05	5,93
19	9,07	,10	22,58	51,08	,13	4,04	,05	6,23
20	8,90	,05	21,68	50,84	,10	5,98	,11	5,24
21	9,05	,03	18,64	51,10	,09	4,20	,14	5,67
22	9,25	,05	17,09	52,22	,07	7,01	,08	5,88
26	9,07	,16	21,20	52,13	,12	4,58	,12	5,11
60	8,98	,08	16,62	47,69	,22	6,03	,16	5,83
Means	9,01	,07	21,01	50,97	,18	4,29	,15	5,45
			Oxidized Glauconites					
143	5,01	,05	31,49	37,14	,28	4,24	,29	3,67
144	3,93	,13	36,06	34,16	,29	3,94	,35	3,07
145	4,18	,17	41,50	32,60	,36	4,35	,50	2,95
146	2,95	,20	52,37	22,29	,31	3,75	,65	2,70
147	,91	,00	62,21	14,22	,25	3,73	,82	1,75
Means	3,40	,11	44,73	28,08	,30	4,00	,52	2,83

(b) MIXED GLAUCONITE/APATITE PELLETS

Phospho-Glauconite Grains

160	8,63	,13	23,08	46,96	3,16	5,28	1,95	3,98
54	7,50	,05	19,11	47,20	5,02	4,45	3,30	4,20
152	7,90	,13	19,13	47,11	5,46	5,48	3,52	4,72
122	7,66	,19	28,02	43,91	7,57	2,98	5,10	3,72
38	7,18	,02	17,00	41,83	10,33	4,08	6,60	4,06
31	5,98	,40	17,37	39,49	11,57	4,31	7,65	3,56
39	4,99	,46	15,09	37,00	13,11	5,19	8,85	3,23
154	6,59	,22	15,55	38,56	14,28	4,49	9,38	3,94
32	5,54	,22	13,08	35,55	17,33	3,99	12,02	3,43
37	6,06	,32	14,22	33,74	17,09	1,76	12,19	5,01
34	5,68	,67	12,35	32,49	17,77	3,92	11,99	4,15
36	5,78	1,27	13,99	30,71	19,11	1,28	13,36	4,68
35	3,77	,78	9,23	22,84	25,77	4,72	16,40	2,82
2	3,79	,37	9,85	25,68	29,88	3,11	17,27	2,72
Means	5,71	,37	14,37	35,39	16,99	3,63	8,60	3,60

Glauco-Phosphate Grains

Analysis Number	K_2O	Na_2O	Fe_2O_3	SiO_2	CaO	Al_2O_3	P_2O_5	MgO
3	2,05	,48	5,60	15,51	41,58	1,94	25,31	1,58
23	3,22	,44	7,51	23,66	29,44	3,86	24,80	2,08
25	6,24	,30	10,86	25,97	26,04	2,90	19,84	2,35
33	3,88	,44	9,75	24,88	29,03	3,48	19,17	2,31
107	1,35	1,04	5,54	9,36	44,64	,33	27,83	1,17
109	,27	1,27	1,32	2,33	51,74	,43	31,76	,64
110	,90	1,21	2,38	5,97	48,49	1,11	30,40	,82
121	1,16	1,29	3,89	11,46	42,26	3,31	26,01	,86
150	4,23	,49	10,69	24,08	29,66	2,48	19,24	2,38
153	3,10	,46	7,54	18,92	36,07	2,28	23,32	2,09
155	3,49	,23	9,45	21,24	32,16	3,03	20,81	2,01
156	2,84	,24	7,94	18,35	35,71	2,71	22,75	1,82
158	1,51	1,02	3,88	7,50	46,58	1,42	28,91	1,21
159	3,15	,37	9,84	16,80	36,56	1,44	23,29	1,50
Mean	2,57	,81	6,46	17,07	37,56	2,30	24,31	1,59

(c) FORAMINIFERA INFILLINGS

Phosphatic Infillings

9	1,24	,97	3,85	7,94	40,72	1,36	22,97	1,19
105	,34	1,36	,92	2,33	50,83	,56	30,93	,62
157	,35	1,07	4,23	3,24	47,57	1,68	28,15	,77
161	,80	,80	8,45	7,69	39,62	3,70	22,59	1,38
162	,78	,71	1,89	6,25	49,45	1,95	30,64	,95
Mean	,70	,98	3,87	5,49	45,64	1,85	27,06	,98

Ferrugineous Phosphatic Infillings

111	1,21	,74	33,96	11,11	23,07	5,83	15,11	1,86
113	,41	,85	35,58	4,47	26,68	3,87	17,82	1,50
116	,96	,70	36,51	8,75	23,48	5,20	15,98	1,71
117	,89	,80	34,59	8,44	24,01	5,12	15,87	1,62
Mean	,87	,77	35,16	8,19	24,31	5,01	16,20	1,67

Phospho-Glauconitic Infillings

106	5,13	1,06	17,68	39,59	16,14	6,48	10,30	3,19
136	4,65	,54	14,26	30,01	20,74	2,43	15,74	3,02
163	4,39	,44	18,77	26,61	23,37	5,36	5,09	2,35
74	5,17	,37	17,33	33,65	17,33	2,98	11,57	2,76
Mean	4,84	,60	17,01	32,47	19,40	4,31	10,68	2,83

Glauconitic Infillings

59	5,98	,06	20,24	17,89	,54	6,70	,16	4,53
61	8,87	,08	18,21	50,18	,88	6,41	,66	5,43
62	5,92	,05	20,15	45,21	5,02	6,14	,35	4,21
Mean	6,92	,06	19,53	47,76	2,15	6,42	,39	4,72

(d) ALTERED FAECAL PELLETS

Glauconitic Faecal Pellets

Analysis Number	K_2O	Na_2O	Fe_2O_3	SiO_2	CaO	Al_2O_3	P_2O_5	MgO
98	8,56	,12	19,15	54,15	,48	5,92	,25	4,91

Glauco-Phosphatic Faecal Pellets

96	1,35	,87	6,34	10,54	43,11	1,36	26,79	1,10
97	1,72	,98	7,41	13,17	40,55	2,12	25,38	1,19
Mean	1,54	,93	6,83	12,35	41,83	1,74	26,08	1,15

Phosphatic Faecal Pellets

99	,03	1,13	,18	,00	53,73	,04	32,71	,72
100	,07	,98	,56	,35	51,45	,04	31,98	1,07
101	,01	1,39	1,93	,08	52,76	,05	31,19	,58
102	,03	1,42	1,73	,10	52,38	,07	30,90	,52
127	,06	1,30	,28	,04	50,28	,00	32,67	,54
128	,08	,88	,21	,11	51,59	,05	35,08	,82
129	,12	,95	1,17	,44	49,41	,07	33,66	,57
130	,08	1,18	,50	,02	48,65	,04	32,78	,61
Mean	,06	1,15	,82	,14	51,28	,05	32,62	,68

(e) PHOSPHORITES MATRICES

Light Brown Phosphatic Matrix

78	,53	1,30	,88	8,41	43,32	2,36	28,06	,94
79	,42	1,20	,76	8,32	45,40	1,79	28,93	,87
80	,60	1,30	,94	9,55	43,73	2,45	27,70	,88
82	,62	1,30	,94	6,54	48,34	2,39	29,29	,75
104	,36	1,08	,62	5,79	49,09	1,34	27,87	,74
119	,33	1,35	,88	4,25	49,03	1,06	30,51	,75
137	,51	,97	1,65	3,49	47,69	,57	31,93	,72
123	,61	1,65	1,29	7,23	45,30	2,94	28,53	,89
124	,58	1,86	1,10	12,16	42,80	3,73	26,54	,80
108	,49	1,14	4,92	4,86	47,31	1,16	29,93	,76
Mean	,51	1,32	1,40	7,06	46,20	1,98	28,93	,81

Lime Green Glauco-Phosphatic Matrix

75	2,19	,75	7,05	28,69	30,25	1,69	19,83	1,41
76	3,14	,78	9,44	20,80	31,90	2,71	20,43	1,80
77	3,08	,80	9,31	20,76	31,71	2,74	20,63	1,84
120	1,57	1,06	5,37	10,48	43,59	1,60	25,44	1,07
Mean	2,50	,85	7,79	20,18	34,36	2,19	21,58	1,53

Colourless Collophane Matrix

Analysis Number	K_2O	Na_2O	Fe_2O_3	SiO_2	CaO	Al_2O_3	P_2O_5	MgO
114	,18	1,05	,48	3,91	49,87	,97	30,77	,49
115	1,68	1,11	6,22	13,55	39,18	2,80	24,83	1,23
112	,25	1,14	,47	3,40	49,38	1,09	30,66	,54
Mean	,70	1,10	2,39	6,95	46,14	1,62	28,75	,75

Average for all three types of matrix.

1,01	1,17	3,08	10,13	43,41	1,96	27,17	,97

High Silica Phosphate Matrix

149	,62	,76	2,30	13,28	42,28	2,19	27,93	,88
118	,61	2,27	,95	26,20	34,78	4,67	21,99	,69
103	,37	1,11	,50	11,43	46,30	1,14	28,37	,75
81	,41	,84	,64	33,49	31,71	1,44	19,09	,43
Mean	,50	1,25	1,09	21,10	38,77	2,36	24,35	,69

Glauconitic and Apatitic Veins

139	,05	,77	,09	,27	51,29	,18	32,07	,60
141	,03	1,07	,23	,21	50,94	,18	31,79	1,04
132	2,50	,58	8,57	21,81	30,79	2,10	21,89	1,95
133	3,22	,30	10,95	20,20	30,50	,91	21,62	2,12
131	6,06	,30	20,22	38,79	11,36	2,20	7,96	3,62
134	7,60	,15	24,33	48,35	1,99	2,50	1,49	4,51
135	6,57	,20	22,20	49,13	4,61	1,86	3,19	3,62
138	7,77	,17	25,70	46,95	1,18	3,97	,87	4,97
140	4,90	,42	16,14	27,96	22,06	2,02	14,61	2,99

(f) PELLETAL PHOSPHORITE

Pelletal Phosphorite

182	,47	,55	14,37	7,16	35,42	2,21	31,17	1,22
183	,80	,84	3,17	3,80	53,52	,54	34,78	1,14
184	1,54	,58	8,93	17,91	33,08	2,64	26,13	1,24
185	,62	,73	5,54	5,96	43,70	1,33	32,94	1,17
186	,31	1,21	3,80	3,44	45,18	1,87	34,55	1,19
187	,21	1,04	2,45	2,06	48,38	,84	35,87	,94
188	,35	,97	1,92	3,39	47,73	1,41	35,95	1,02
189	,34	,87	1,48	4,15	48,18	1,57	35,76	,95
190	,16	,90	1,20	2,23	48,34	,79	35,94	,93
191	,86	,86	7,03	6,48	42,49	,82	32,33	1,19
192	,65	,92	2,36	5,76	46,87	1,30	35,07	1,26
194	,35	,61	2,78	3,77	45,90	1,50	34,74	,99
Mean	,56	,84	4,59	5,51	44,90	1,40	34,00	1,10

B(v) Results of Microprobe Analyses of onland phosphorites

Matrices of Quartzitic Phosphorites

Analysis Number	K_2O	Na_2O	Fe_2O_3	SiO_2	CaO	Al_2O_3	P_2O_5	MgO
Saldanha Formation:								
165	,42	,19	2,31	6,58	46,61	1,52	31,90	,58
168	,05	,21	,56	,44	50,51	,37	35,56	,25
176	,17	,18	1,10	2,25	48,66	,88	36,80	,28
Mean	,21	,19	1,32	3,09	48,59	,92	34,75	,37
Varswater Formation:								
205	,21	,53	3,05	1,95	50,43	1,33	36,03	,42
206	,12	,21	,47	1,06	49,13	1,32	36,05	,20
Mean	,17	,37	1,76	1,56	49,78	1,33	36,04	,31
Skoongesig Phosphatic Sandstone:								
195	,37	,28	1,43	6,03	45,56	5,46	35,33	,34
198	,30	,00	1,02	5,97	46,59	4,41	35,99	,31
Mean	,34	,14	1,23	6,00	46,03	4,94	35,66	,33

Pebble Inclusions in the above Matrices

Saldanha Formation:								
204	,23	,51	2,02	3,11	51,31	1,06	36,66	,13
207	,49	,58	2,91	19,20	40,81	2,44	30,82	,54
Mean	,36	,55	2,46	11,16	46,06	2,05	33,79	,34
Varswater Formation:								
166(1)	3,13	,31	23,57	22,78	19,55	2,72	15,11	2,17
167	,58	,56	4,82	5,86	45,49	,99	31,43	1,05
169	,08	,56	2,27	,77	51,70	,70	34,80	,35
170	,20	,53	2,14	1,48	50,84	1,14	33,86	,39
172	,28	,35	2,97	3,56	49,98	1,74	35,68	,56
181	,57	,35	4,25	5,48	47,10	1,64	36,01	,97
Mean	,34	,47	3,29	3,43	49,02	1,24	34,36	,66
Skoongesig Phosphatic Sandstone:								
196	,73	,09	8,40	9,21	32,69	10,54	31,26	,45
200	,56	,09	9,64	8,42	31,53	11,18	30,54	,51
201	,55	,09	6,33	8,19	36,38	8,94	32,93	,45
Mean	,61	,09	8,12	5,54	33,53	10,22	31,57	,47

(1) Not included in mean values.

B(vi) Microanalyses of Phosphorite Matrices, Phosphate Pellets and Pelletal Phosphorites (See Section 5.4.9(c))

Sample Number	Station Number	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	Na_2O	P_2O_5	SO_3	S	Na
(a) Phosphorite Matrices												
1	2495B	2,63	1,05	,45	,55	50,65	,18	1,31	32,82	1,90	,77	,97
2	2495B	4,24	1,61	,61	,58	49,39	,30	1,21	30,91	1,93	,78	,90
5	310	2,41	,98	,80	,70	51,96	,16	1,78	31,06	2,66	1,08	1,32
6	310	3,88	2,61	,72	,67	47,04	,37	1,31	25,35	2,00	,81	,97
7	2254	4,34	1,88	,59	,98	49,33	,30	1,17	29,52	1,66	,67	,87
9	514	5,31	1,56	1,52	,70	48,47	,48	1,31	27,74	1,87	,76	,97
10	514	2,76	,66	1,17	,52	49,90	,30	1,48	30,05	2,06	,84	1,10
11	2254	3,61	1,18	,61	,79	49,08	,43	1,44	30,59	1,82	,74	1,07
13	2495	4,98	1,45	,67	,52	48,42	,48	1,26	30,48	1,85	,75	,93
14	2688	3,84	1,41	,66	,83	52,82	,32	,99	20,88	1,47	,60	,73
16	510	5,02	1,86	,69	,90	47,58	,47	1,32	28,71	1,96	,79	,98
18	2254	3,56	1,38	,72	,90	49,17	,41	1,37	28,73	1,87	,76	1,02
20	2254	5,15	1,82	,96	,91	48,98	,57	1,20	25,46	1,27	,51	,89
22	2254	7,71	1,98	,93	,98	47,66	,54	1,09	27,95	1,72	,70	,81
(b) Phosphate pellets												
3	2495B	,10	,07	2,54	,61	50,16	,07	1,43	29,48	5,52	2,23	1,06
8	2254	,15	,05	,80	,92	53,65	,05	1,03	30,87	2,67	1,08	,76
12	2495	,12	,09	2,93	,63	50,20	,00	1,95	31,26	4,67	1,89	1,45
15	510	,10	,04	,36	,65	51,68	,04	1,29	31,85	3,67	1,49	,96
17	2254	,83	,09	,69	,64	52,98	,14	1,13	29,14	2,61	1,06	,84
19	2254	,02	,04	,19	,75	54,83	,06	1,30	31,88	2,37	,96	,96
21	2254	,27	,07	1,06	,89	53,27	,54	1,17	30,39	2,69	1,09	,87
23	2254	,04	,09	,46	,60	49,96	,03	1,10	31,56	2,73	1,09	,82
24	2254	,08	,05	,46	,54	50,85	,00	1,18	31,23	2,62	1,03	,88
25	2495	,10	,13	2,27	,60	47,45	,04	1,60	20,64	4,47	1,79	1,19
26	2495	,08	,13	2,16	,58	47,10	,04	1,14	29,91	4,62	1,85	,85

Sample Number	Station Number	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	Na_2O	P_2O_5	SO_3	S	Na
Phosphate pellets (contd)												
27	310	,04	,04	,28	,62	51,15	,02	1,01	32,28	2,97	1,19	,75
28	310	,00	,07	,19	,54	49,63	,03	1,31	30,69	3,05	1,22	,97
29	310	1,64	,05	1,32	,64	49,14	,34	1,05	31,02	2,87	1,15	,78
31	310	,02	,00	,13	,52	50,78	,06	1,15	31,09	3,10	1,24	,85
32	310	,02	,27	,14	,52	50,11	,04	1,22	32,25	2,84	1,14	,91
33	310	,02	,02	,24	,70	51,00	,07	1,22	31,79	3,54	1,42	,91
44		,00	,04	,00	,13	51,63	,05	1,32	32,40	3,42	1,37	,98
45		,00	,02	,38	,67	52,19	,06	1,34	32,77	3,44	1,38	,99
(c) Pelletal Phosphorite												
34		4,91	1,47	1,39	,97	44,54	,41	,94	29,84	4,61	1,85	,70
35		2,35	1,13	,80	,89	47,15	,20	1,04	31,37	3,10	1,24	,77
37		1,50	,64	,88	,93	51,34	,09	,84	31,66	3,60	1,44	,62
38		2,93	1,15	1,57	,87	47,82	,27	,87	30,42	4,97	1,99	,65
39		3,72	1,63	1,43	,84	47,90	,40	,85	27,51	4,28	1,71	,63
41		8,04	1,85	2,63	1,34	44,05	,93	,80	28,75	2,28	,91	,59
42		2,85	1,28	2,97	,94	45,19	,30	1,31	28,68	8,27	3,31	,97
43		9,74	2,15	3,17	1,52	42,80	,86	,80	27,40	2,25	,90	,59

IV - C. X-ray diffraction determination of CO_2 in the apatite phase of onland and off-shore phosphatic material.

Sample	Class	2θ (004)-(410) (in degrees)	% CO_2
Marine Phosphorite Rocks:			
1706	NI	1,22	5,2
2461	NI	1,18	6,1
2703	NI	1,27	4,8[1]
1692	NII	1,34	3,9
1700	NIII	1,22	5,5
2220	NIII	1,20	5,9
2254	NIII	1,26	5,6
2495	NIII	1,24	5,3
310	NIII	1,25	5,2(5,3)[2]
1706	CI	1,23	5,5
2240	CI	1,26	5,1
2786	CI	1,22	5,6
2254	CII	1,19	6,0
2487	CII	1,21	5,9
2449	Miscell.	1,21	5,9
2460	Miscell.	1,25	5,2
		Average	5,53

Sample	Type of Material	2θ (004)-(410)	% CO_2
Marine Pelletal Phosphorites:			
269	Pellets	1,35	3,7
3346	Pellets	1,34	3,9
2464	Infillings	1,37	3,4
On-shore Phosphorite Rocks:			
Site 1	Phos.sst.	diffuse peaks	
3	Phos.sst.	1,42	2,60
5	Phos.sst.	diffuse peaks	
6	Phos.coquina	diffuse peaks	
7(B)	Phos.sst.	1,42	2,60
7(E)	Phos.sst.	1,45	2,25
9	Phos.sst.	1,46	2,10
		Average	2,39

1. The accuracy of this value is doubtful because the peaks were diffuse.
2. Figure in parenthesis is value determined by Parker (1971) for the same rock.

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PLATE I - 1

Plate I-1. Examples of echo-sounder records

A. Three types of sea floor are depicted in this echogram. (1) the rocky nearshore platform (note the presence of a second order multiple), (11) the inner shelf sand blanket, (111) a sediment-free phosphorite bedrock on the outer shelf, (1V) a smooth cover of sediment on the slope. The Cape Canyon is also shown.

B.& C. The sediment-free, rocky outer shelf. Bedrock is composed of phosphatized limestones. C shows a small upper slope slump nick.

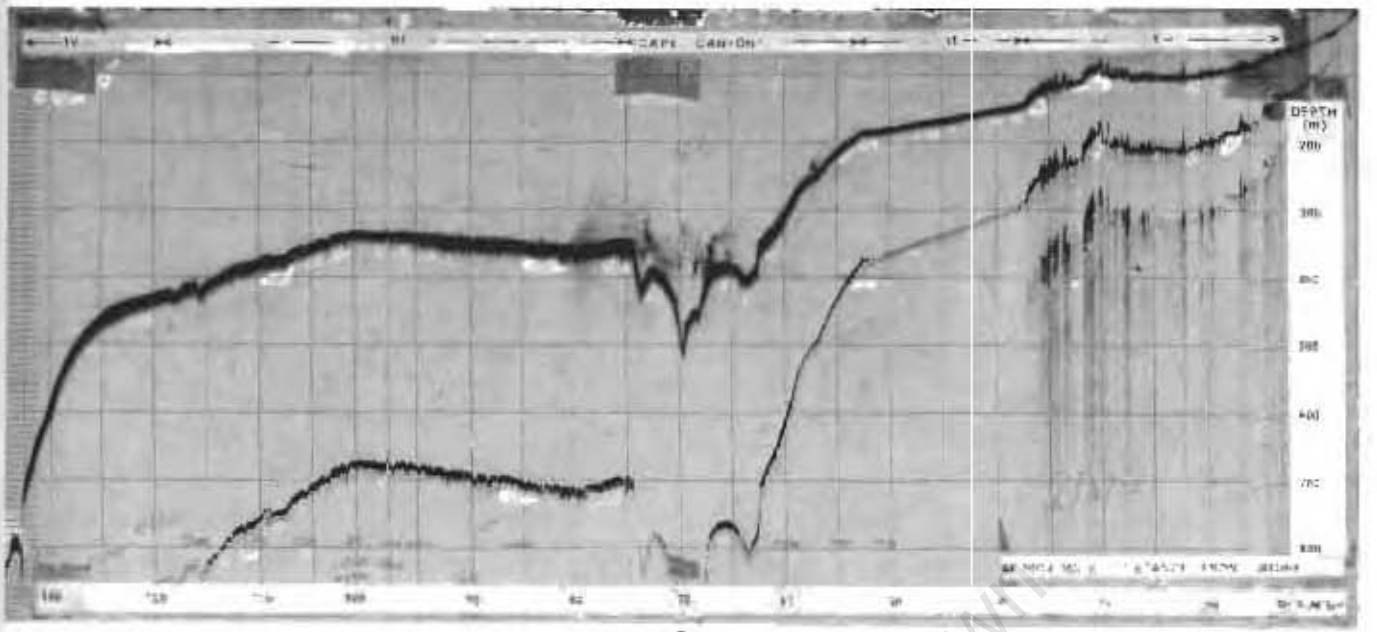
D. Echo-sounder trace depicting extremely poorly-compacted mud located at the base of the rocky coastal platform. Sound is reflected from both the upper water-mud and the lower mud-sand interfaces.

E. Echogram record of the coastal rocky platform, and the shoreward edge of inner shelf sand blanket.

F. The seaward edge of the inner shelf sand blanket as it wedges out onto the sediment-free rocky mid shelf.

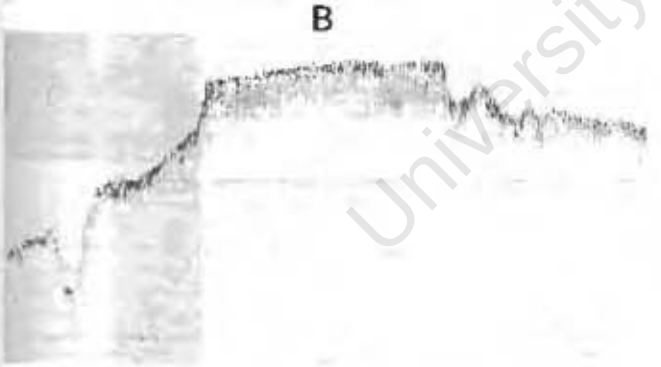
G. Flat-lying phosphorite bedrock on the shelf dissected by shallow (5-10 m) valleys. Residual glauconite commonly occurs in such hollows.

H. "V"-shaped valleys, exhibiting levees (4 m above the surrounding floor) have been eroded into unconsolidated sediment on the outer shelf off the Berg River. These morphological features are probably the heads of slump nicks.

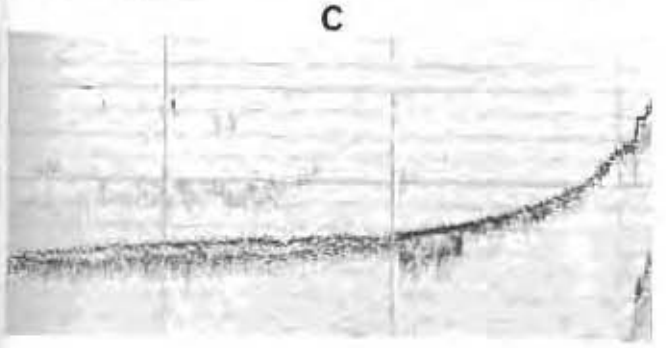


A

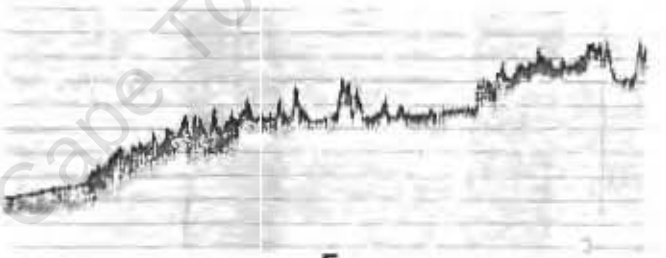
B



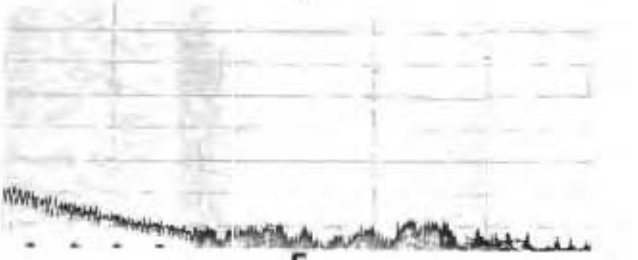
C



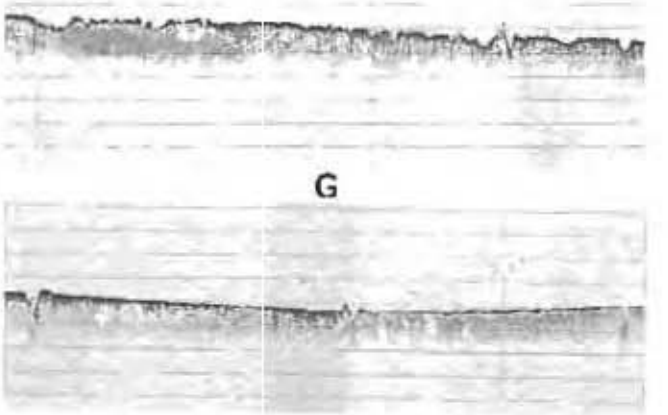
D



E



F



G

H

Vertical scale 10m. per interval

Approximate horizontal scale 2,6cm = 1 n. mile

Plate I-1

PLATE I - 2

Plate I-2. Sea-floor photographs

The size of objects in the photographs may be estimated by comparing them to the compass, which is 10 cm in diameter and is suspended 1 metre above the bottom.

A. Nearshore rocky platform (50 m):
The rocky platform mantled with gravelly quartzitic sand and boulders.

B. Relict, highly glauconitic sands covering the rocky outer shelf (240 m):
Well compacted, residual glauconitic (70%) sand on the rocky mid shelf west of Cape Town.

C. Rocky outer shelf with intermittent sediment cover (240 m):
Foraminiferal sand (80% $CaCO_3$) filling depressions on the mid shelf off the Olifants River mouth. Alcyonarians in the photograph suggest a thin sediment cover.

D. Rocky outer shelf (302 m):
A veneer of glauconitic (65%) sand covers phosphorite on the outer shelf west of Cape Town. Moderate (34% $CaCO_3$) carbonate deposition occurs on the outer shelf in this region. The sea-fan indicates a south-eastward moving bottom current operating along the shelf break. Brittle stars are common.

E. Rocky mid shelf (190 m):
The rocky shelf south of False Bay covered by a thin veneer of terrigenous sand which has been diluted by foraminifera (45% $CaCO_3$).

F. Continental slope sediment (1136 m):
The sea-floor in the Cape Point Valley covered with silt-sized quartz (50%) and foraminiferal tests (48% $CaCO_3$). Glauconite occurs as a minor constituent (2%). Numerous burrows rimed with lighter material indicates active bioturbation by abundant infauna.

A

B

C

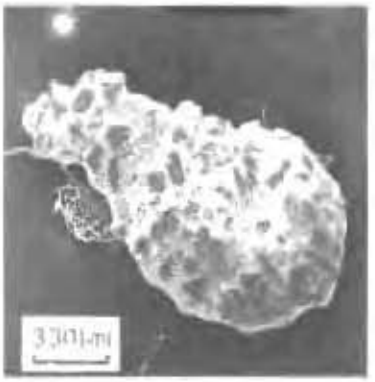
D

E

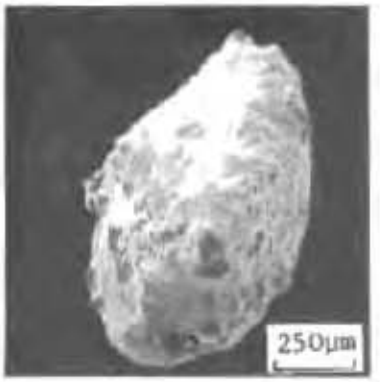
F

AGGLUTINATED FORAMINIFERA

CYCLAMMINA cf. CANCELLATA



DISCAMMINA Sp.

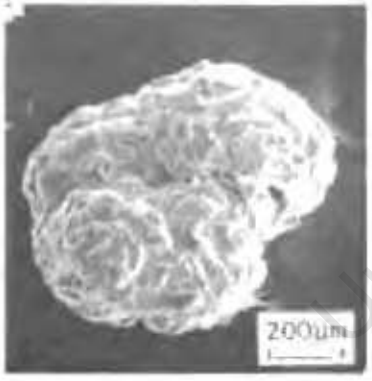


SIGMOILOPSIS Sp.

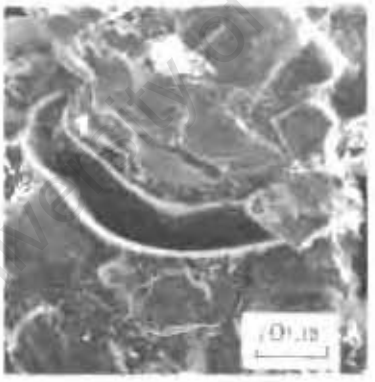
MARTINOTTIELLA COMMUNIS

MARTINOTTIELLA COMMUNIS

(?)MIGROS Sp.

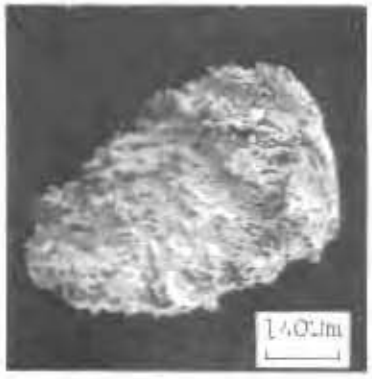


HAPLOPHRAGMOIDES
cf. SPHAERILOCULUM

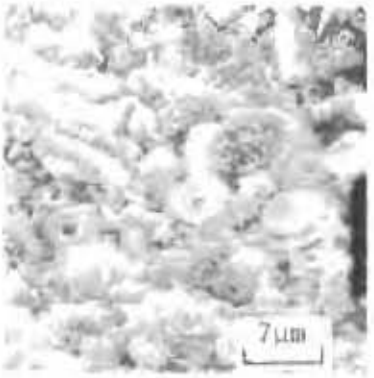


HAPLOPHRAGMOIDES
cf. SPHAERILOCULUM

(?)GAUDRYINA Sp.



SIPHOTEXULARIA CONCAVA



SIPHOTEXULARIA CONCAVA

(?)REOPHAX AGGLUTINATUS

PLATE IV - 1

Plate IV-1. Glauconite types

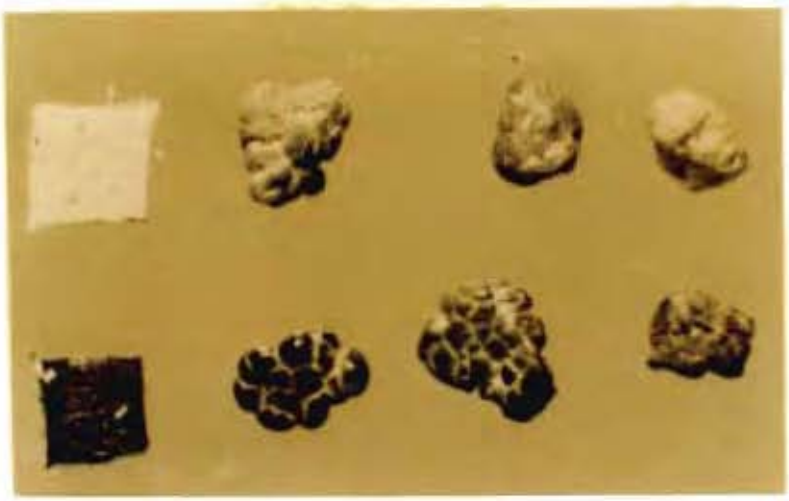
A. Lobular and highly sutured pellets ranging from yellow-green to light green to black (reference block : black, NI, approximate size 0,5 mm square).

B. Foraminiferal infillings (probably of Globigerina sp. and Orbulina sp.)

C. Oxidized glauconite grains. The three pellets on the left hand side of the illustration are completely altered, but the grain on the right exhibits an oxidized margin. The associated change in composition can be judged from the micro-analyses recorded below:

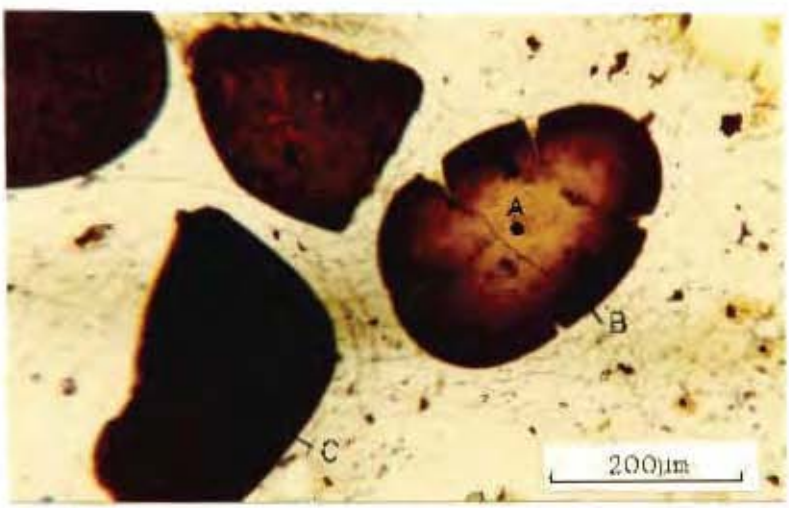
ANALYSES

	A	B	C
SiO_2	48,13	37,14	22,29
Al_2O_3	3,60	4,24	3,75
Fe_2O_3	27,07	31,49	52,37
MgO	3,83	3,67	2,70
CaO	0,14	0,28	0,31
Na_2O	0,57	0,05	0,20
K_2O	6,75	5,01	2,95
P_2O_5	0,14	0,29	0,65
Total	90,23	82,17	85,22



A

B



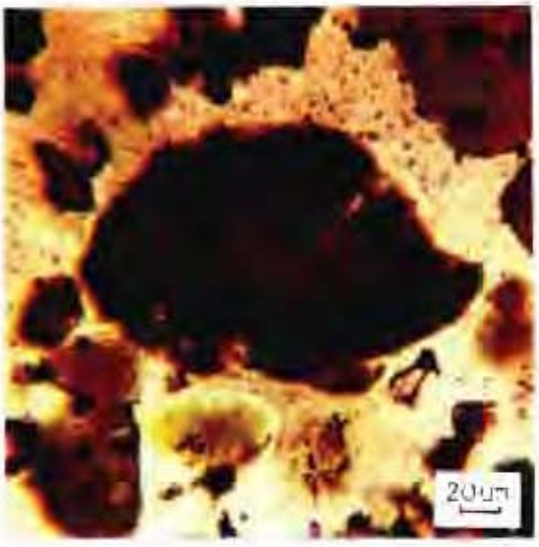
C

Plate IV-1

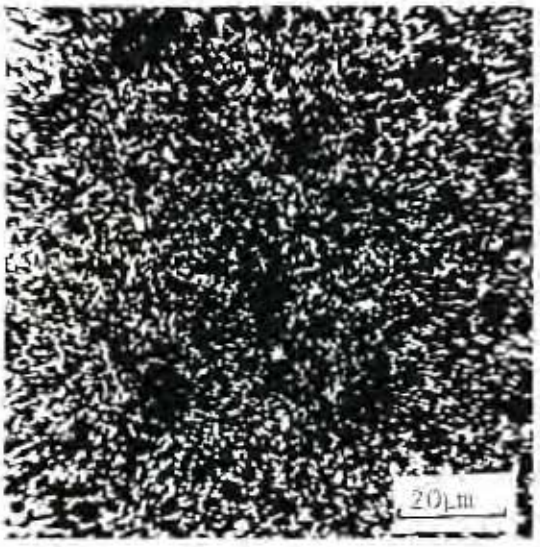
PLATE IV - 2

Plate IV-2. An immature glauconite pellet with inclusions of calcium carbonate

The immature glauconite grain shown opposite contains small (< inclusions of calcium carbonate which may alter to carbonate fluorapat: to form a mixed glauconite/apatite pellet, see Plate IV-11.



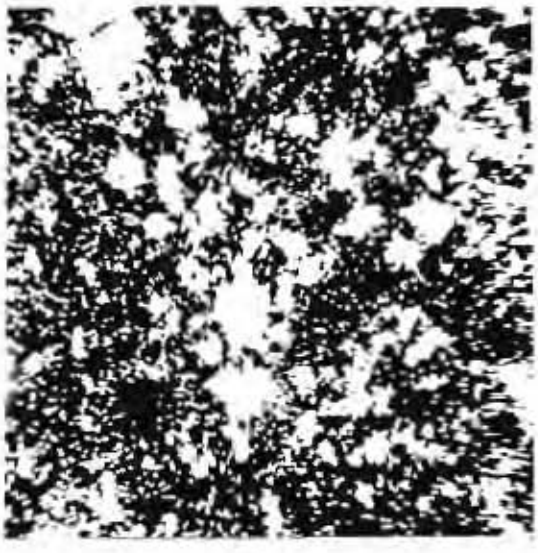
Photomicrograph



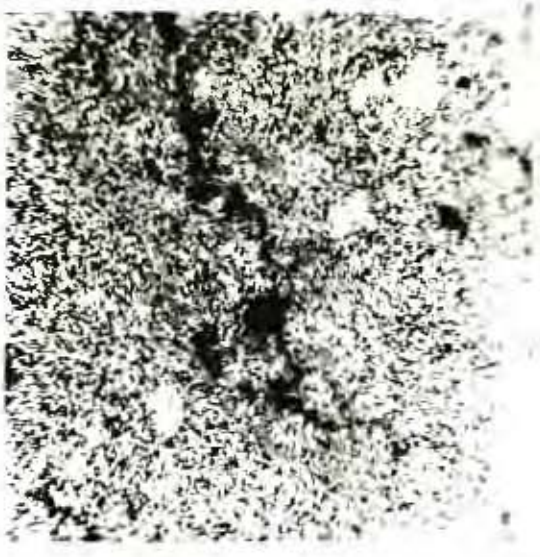
Fe

P

K



Ca



Si

Plate IV-2

PLATE IV - 3

Plate IV-3. NI, NIII and CI class phosphorites

NI class phosphorite:

A. This tabloid-shaped foraminiferal packstone shows phosphatized upper and lower margins.

B. NI phosphorites contain mainly broken and intact foraminiferal tests, very fine quartz and a micrite/collophane cement.

NIII class phosphorites:

C. The nearshore phosphorite shown opposite contains a heterogeneous mixture of well-rounded quartz pebbles, glauconite, rock fragments and very fine quartz.

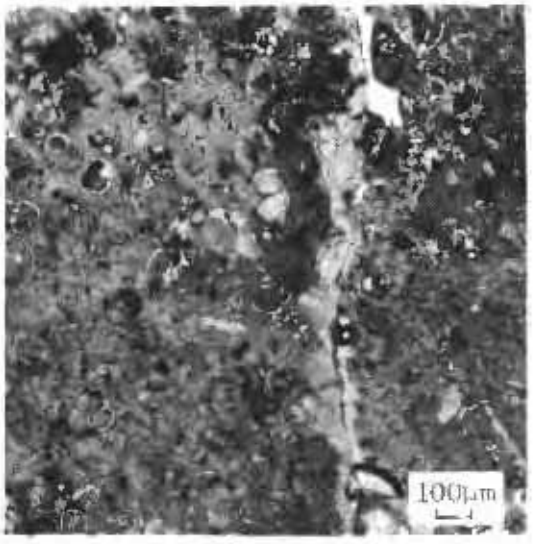
D. Collophane cements a poorly sorted mixture of very fine quartz and medium sand-sized glauconite. Note that some glauconite grains have a lighter apatitic core and that the pellet in the top left hand corner of the illustration contains silt-sized quartz fragments.

CI class phosphorites:

E. The CI phosphorite seen opposite contains irregular-shaped microfossiliferous pebbles some of which have phosphatized margins. Black glauconite grains and quartz pebbles are clearly visible.

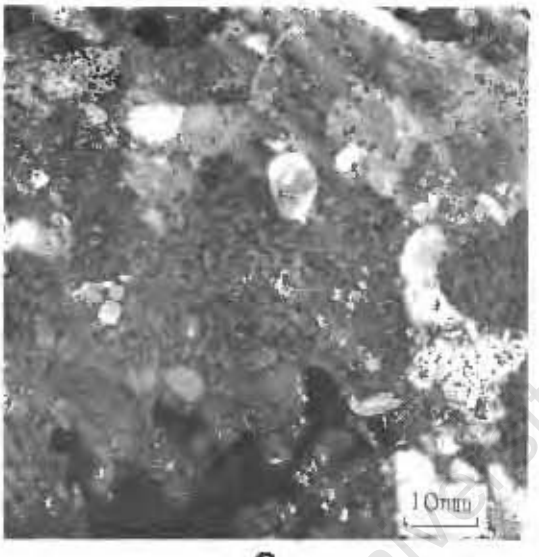
F. The contact between an enclosed microfossiliferous pebble composed of a large irregular quartz grain and abundant foraminifera and a highly glauconitic matrix containing an intact foraminiferal test.

A

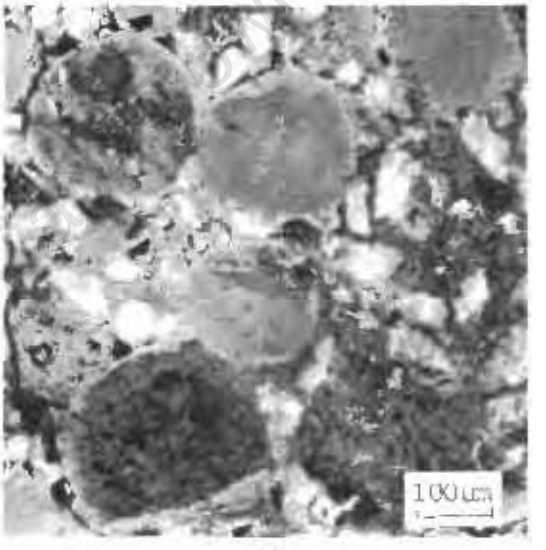


B

NI Class Phosphorite

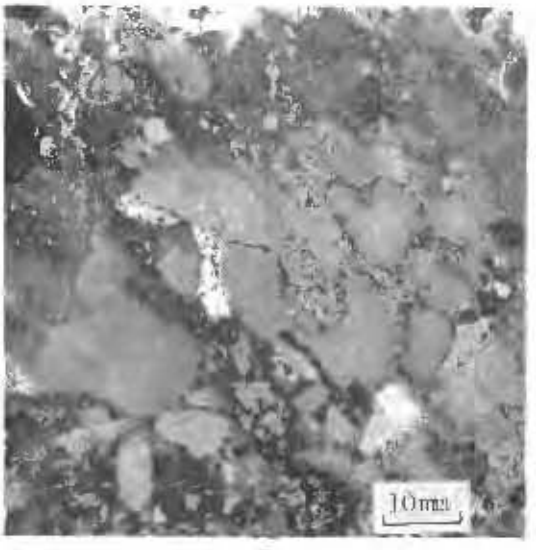


C

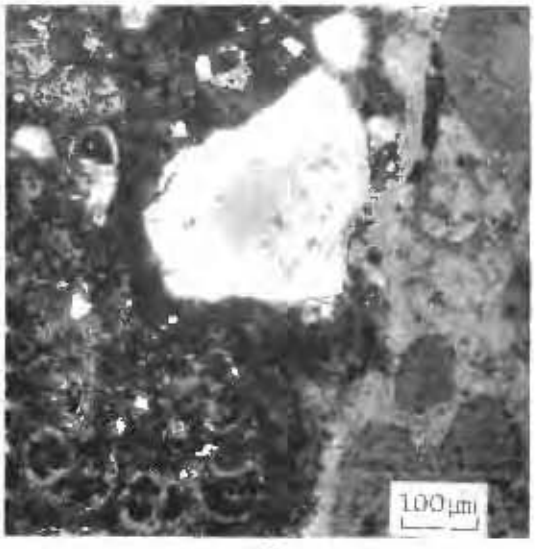


D

NIII Class Phosphorite



E



F

CI Class Phosphorite

PLATE IV - 4

Plate IV-4. A CII phosphorite and onland and off-shore quartzitic phosphorites

CII class phosphorite:

A. Miscellaneous calcareous debris is enclosed in a collophane/goethite cement. Note the fossiliferous pebble inclusions and the glauconite-free matrix.

B. The contact between a microfossiliferous pebble containing calcareous fragments set in a collophane cement and a phosphorite matrix composed of foraminiferal tests and a goethite cement.

Onshore quartzitic phosphorite:

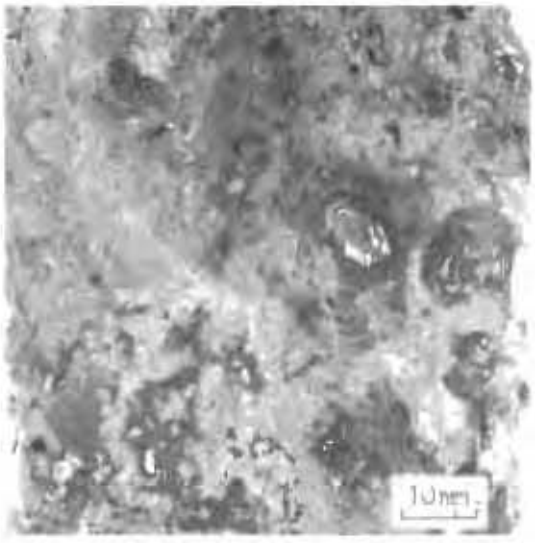
C. An onshore phosphorite exhibiting preferential phosphate mineralization. Note the absence of calcareous material and glauconite.

D. Angular, very fine quartz is a major component of onland phosphorites. Replaced bone (a) and pelletal phosphorite (b) are less common constituents of the basal quartzitic phosphorite of the Saldanha Formation.

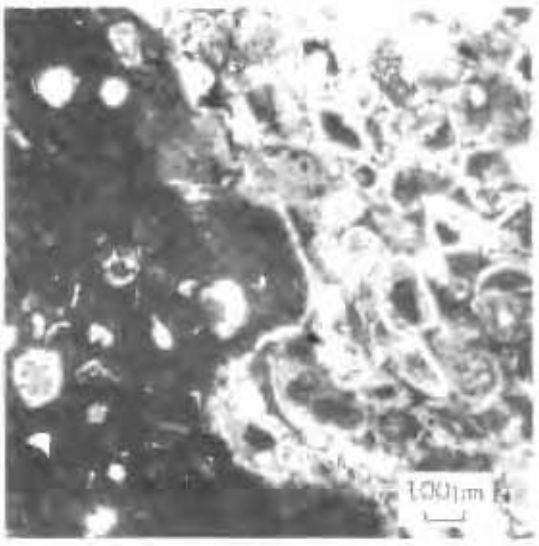
Off-shore quartzitic phosphorite:

E. The appearance of this off-shore quartzitic phosphorite is entirely different to that of the calcareous or glauconitic phosphorites. Instead it resembles very closely phosphorites which have formed by phosphate precipitation and commonly found off the Chilean coast. The insert shows such a phosphorite recovered from the Chilean shelf. (The photograph has been reproduced with the kind permission of Dr. W.C. Burnett).

F. The rock is composed of abundant well-sorted, very fine quartz set in a light brown collophane cement. Note the absence of calcareous material and glauconite.



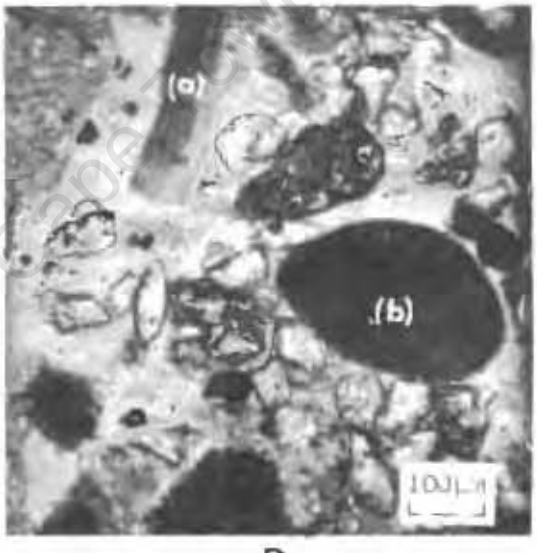
A



B

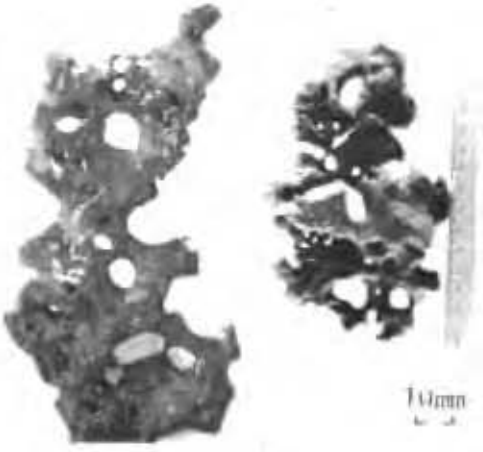
C II Class Phosphorite

C

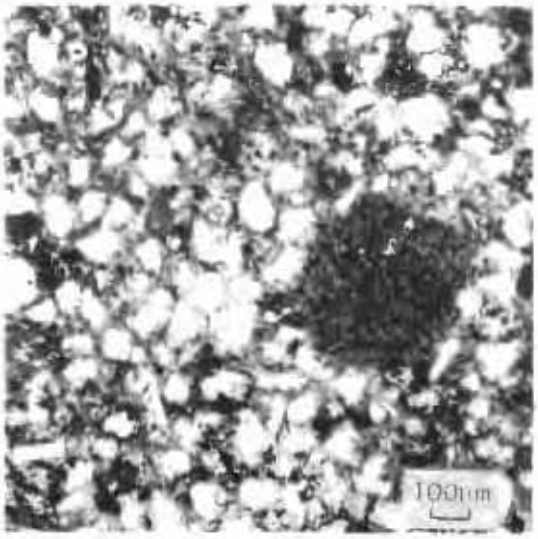


D

Onshore Quartzitic Phosphorite



E



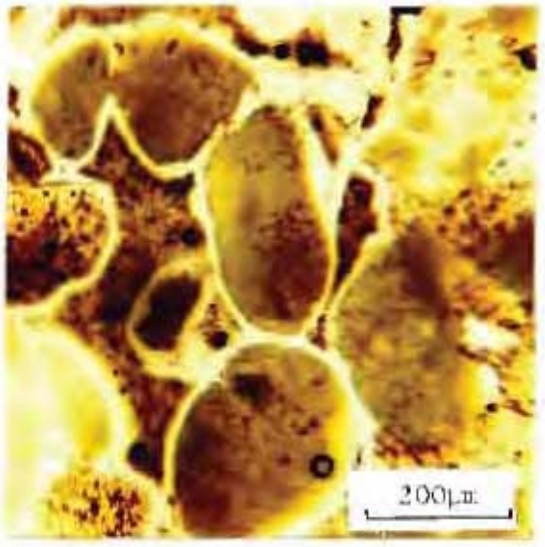
F

Offshore Quartzitic Phosphorite

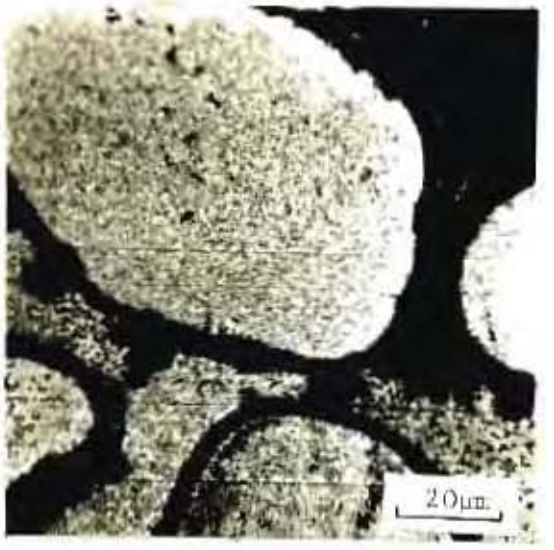
PLATE IV - 5

Plate IV-5. A phosphorite containing phosphatic and glauco-phosphatic matrices

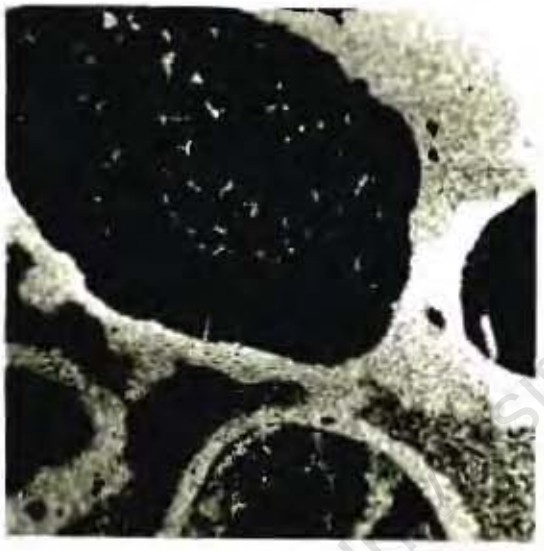
The matrix of an NIII phosphorite rock shown opposite is phosphatic at the top of the illustration, but changes abruptly to a glauco-phosphatic composition towards the lower part of the figure. The centre of the larger glauconite grain is mottled, whereas the radial glauconite/apatite pattern exhibited by the other glauconite pellet is typical of a heterogeneous grain.



Photomicrograph

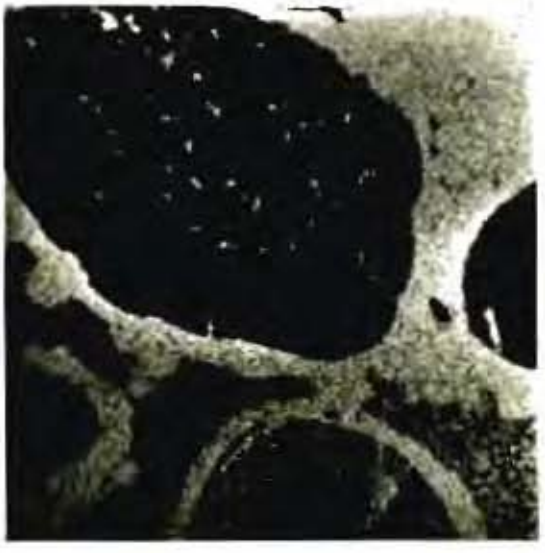


Fe

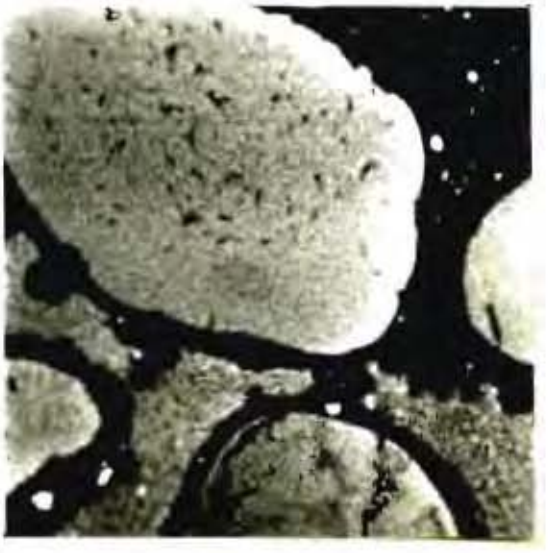


P

K



Ca



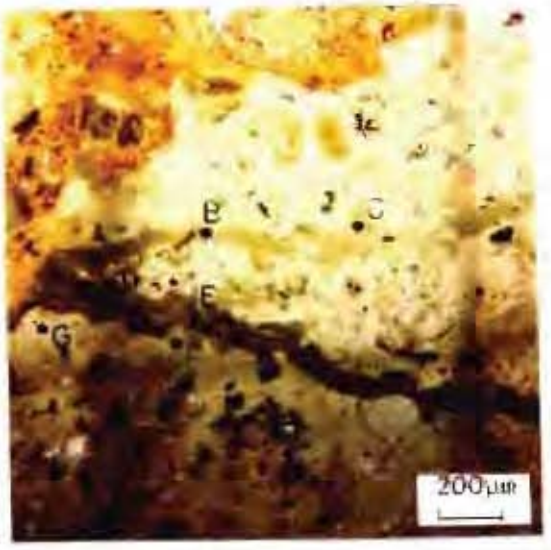
Si

PLATE IV - 6

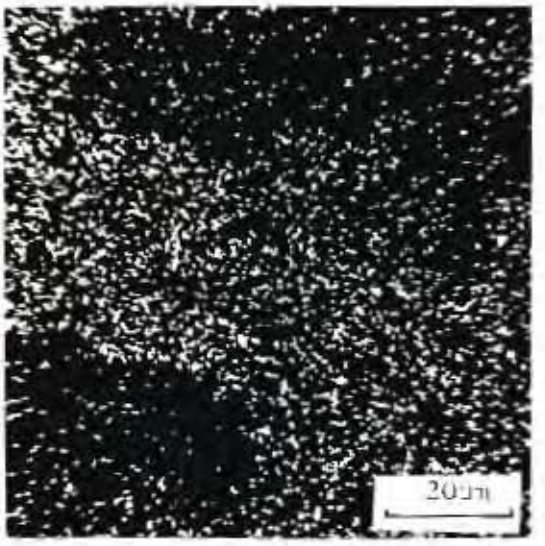
Plate IV-6. A glauconite/apatite vein in an NI phosphorite

Almost pure glauconite was deposited on the walls of the fracture in the phosphorite shown opposite. However, apatite-rich material in the core of the vein indicates that the composition of subsequent solutions permeating through the rock changed. Note that the matrix is composed of a glauconite/apatite mixture.

	ANALYSES						
	A	B	C	D	E	F	G
SiO_2	38,79	21,81	20,20	48,35	49,13	30,01	3,49
Al_2O_3	2,20	2,10	0,91	2,50	1,86	2,43	0,57
Fe_2O_3	20,22	8,57	10,95	24,33	22,20	14,26	1,65
MgO	3,67	1,95	2,12	4,51	3,62	3,02	0,72
CaO	11,36	30,79	30,50	1,99	4,61	20,74	47,69
Na_2O	0,30	0,58	0,30	0,15	0,20	0,54	0,97
K_2O	6,06	2,50	3,22	7,60	6,57	4,65	0,51
P_2O_5	7,96	21,89	21,62	1,49	3,19	15,74	31,95
Total	90,56	90,19	89,82	90,92	91,38	91,39	87,55



Photomicrograph

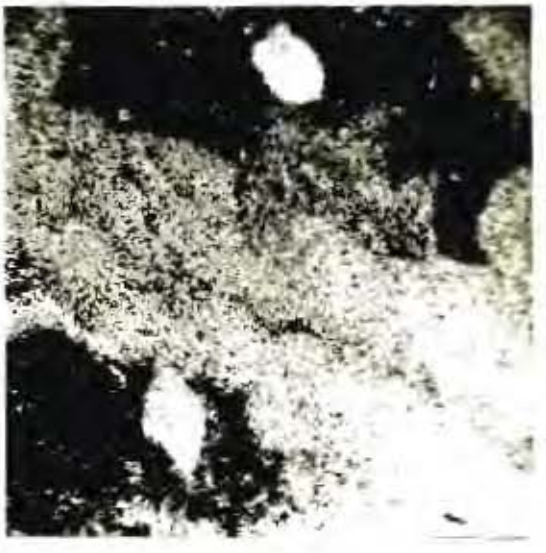


Fe

P

K

Ca



Si

Plate IV-6

PLATE IV - 7

Plate IV-7. Glauconitic and apatitic veins and an Fe-rich phosphatic infilling

A. Glauconitic and apatitic veins.

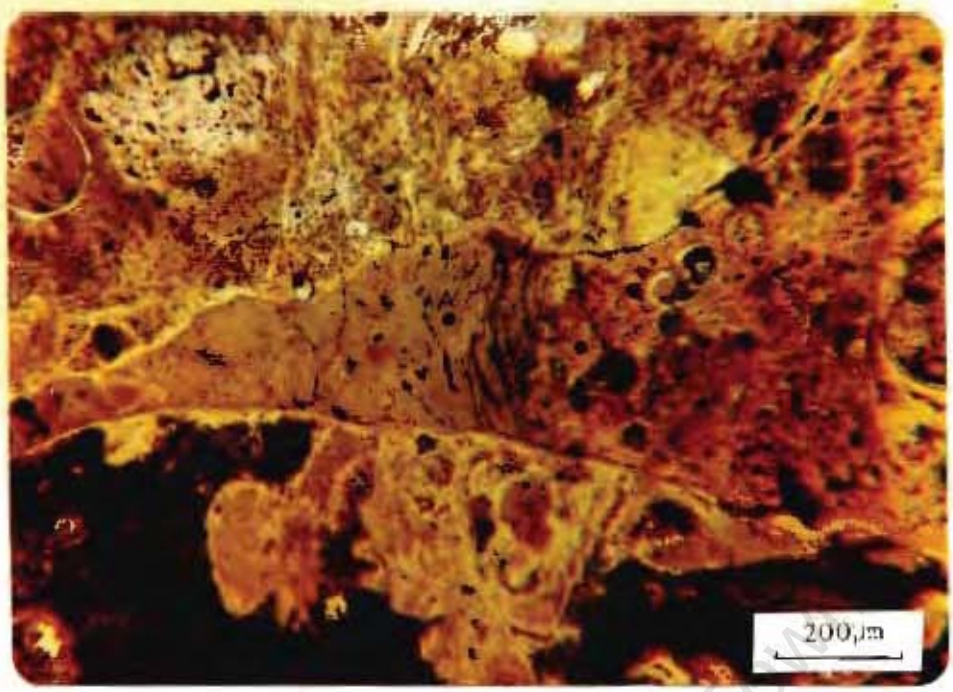
The void between an enclosed pebble and the matrix of the CII class phosphorite shown opposite has been filled with apatite and glauconite during two separate authigenic episodes. The micro-analyses presented below give the composition of the intrusive phases.

	ANALYSES	
	A	B
SiO_2	46,95	0,27
Al_2O_3	3,97	0,18
Fe_2O_3	25,70	0,09
MgO	4,97	0,60
CaO	1,18	51,29
Na_2O	0,17	0,77
K_2O	7,77	0,05
P_2O_5	0,87	32,07
Total	91,58	85,32

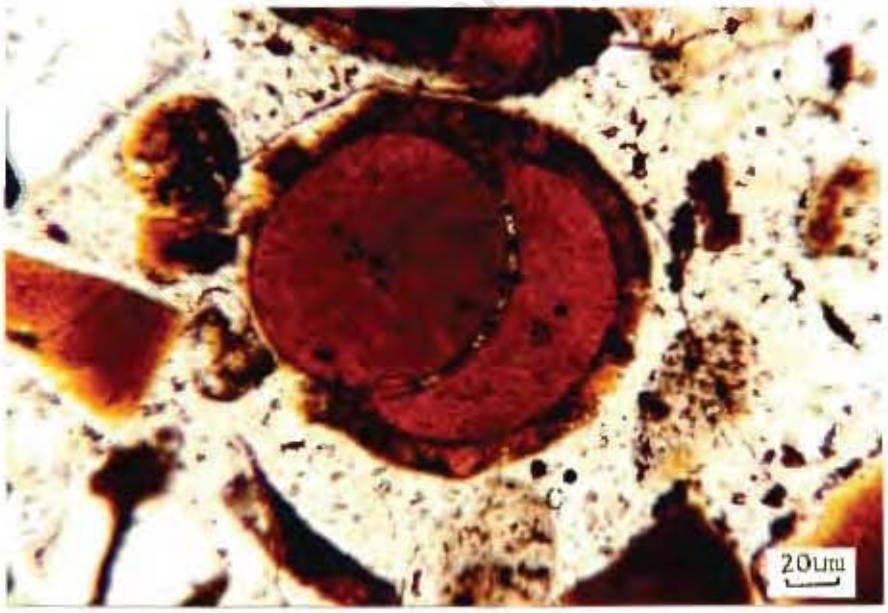
B. An Fe-rich phosphatic infilling.

The Fe content of the phosphatic infilling shown opposite is enriched approximately 60 times relative to the ambient phosphorite matrix. X-ray scans have shown that the Fe is evenly disseminated through the infilling and is not associated with S. The composition of the infilling is recorded below:

	ANALYSES		
	A	B	C
SiO_2	7,66	6,74	3,91
Al_2O_3	5,04	4,91	0,97
Fe_2O_3	32,27	28,75	0,48
MgO	1,73	1,69	0,49
CaO	24,06	26,50	49,87
Na_2O	0,73	0,75	1,05
K_2O	0,86	0,78	0,18
P_2O_5	16,29	17,57	30,77
S	0,54	0,62	0,48
Total	89,10	88,31	88,20



A



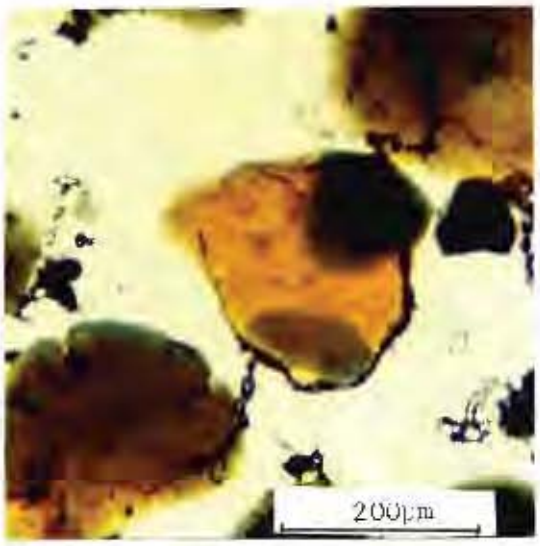
B

Plate IV-7

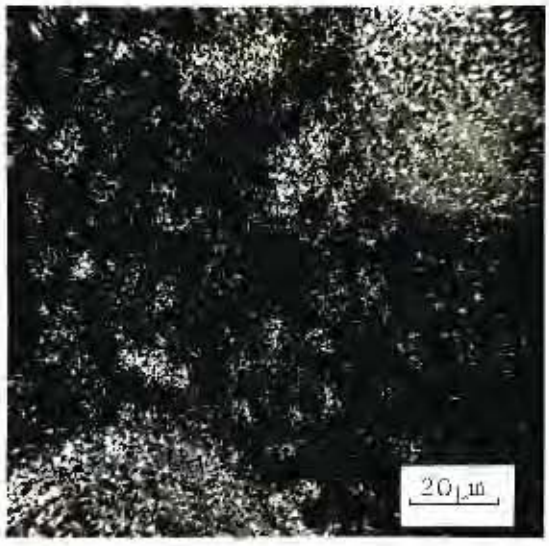
PLATE IV - 8

Plate IV-8. A fragment of glauconite-rich NIII phosphorite

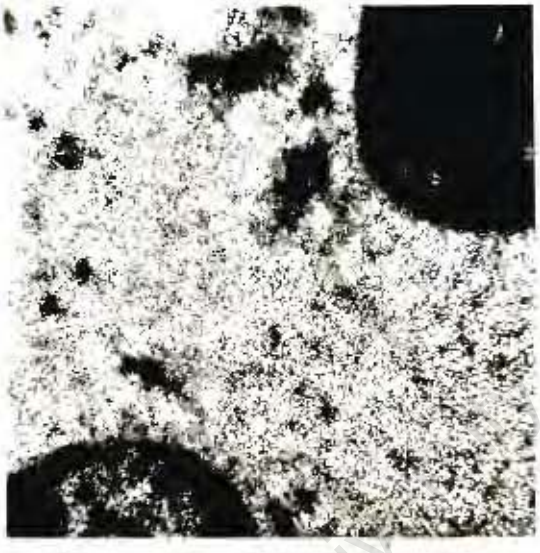
The composite glauconite/phosphorite grain shown opposite is derived by fragmentation of a glauconitic phosphorite rock. Note that the glauconite grain in the left hand bottom corner of the illustration has a composition similar to that of the phosphorite matrix.



Photomicrograph



Fe



P

K

Ca

Si

Plate IV-8

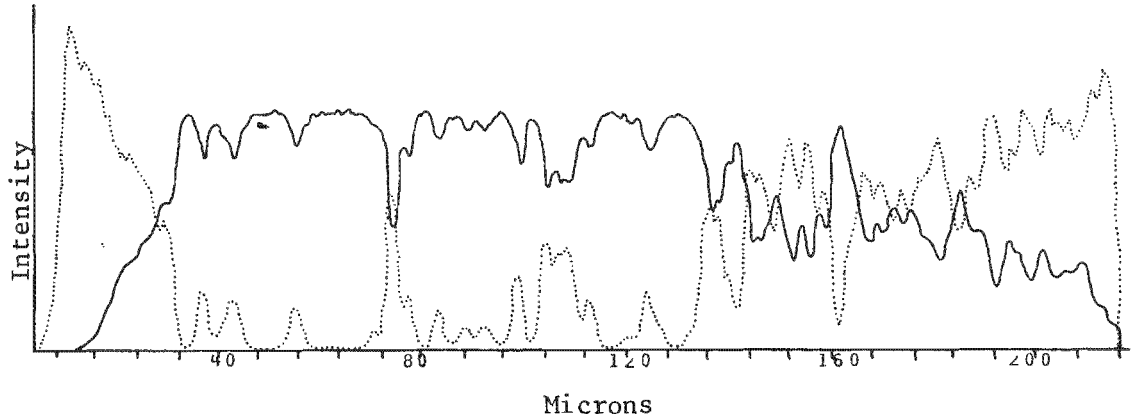
PLATE IV - 9

Plate IV-9. A partially phosphatized glauconite grain

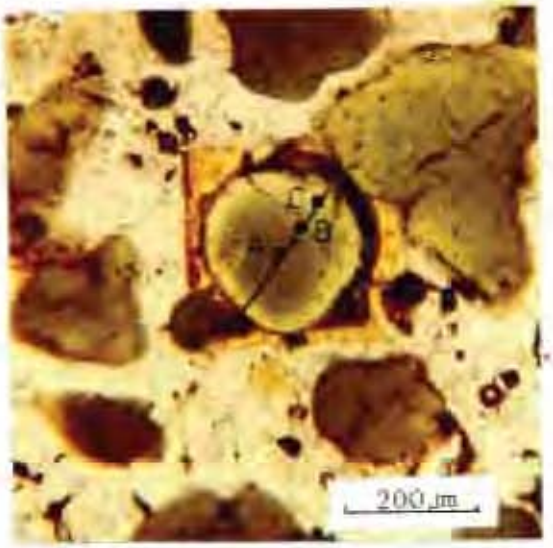
A glauconite pellet with a phosphatized outer margin is shown opposite. Note the compositional changes that occur from the centre of the grain to the rim recorded in the three probe analyses and in the line scan traverse reproduced below.

ANALYSES

	A	B	C
SiO_2	47,11	38,56	18,92
Al_2O_3	5,48	4,49	2,28
Fe_2O_3	19,13	15,55	7,54
MgO	4,72	3,94	2,09
CaO	5,46	14,28	36,07
Na_2O	0,13	0,22	0,46
K_2O	7,90	6,59	3,10
P_2O_5	3,52	9,38	23,32
Total	93,45	93,01	93,78

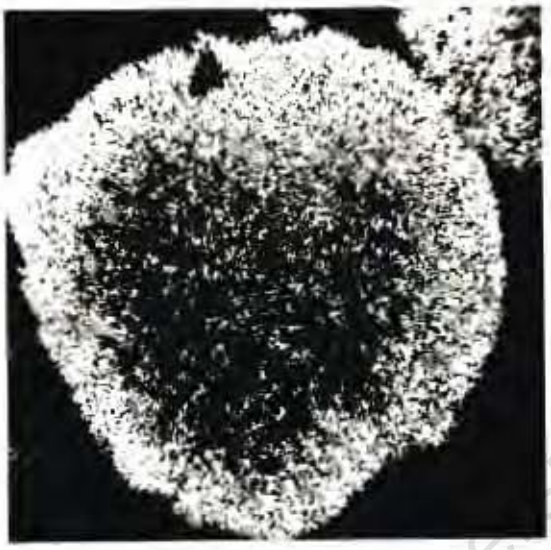


LINE SCAN OF Ca (....) AND Si (____)



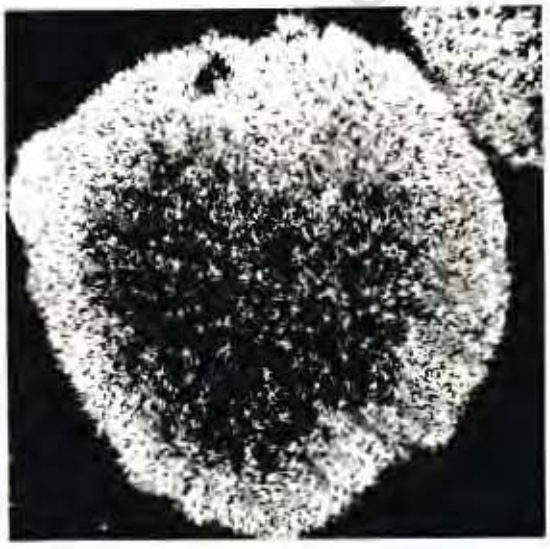
Photomicrograph

Fe



P

K



Ca

Si

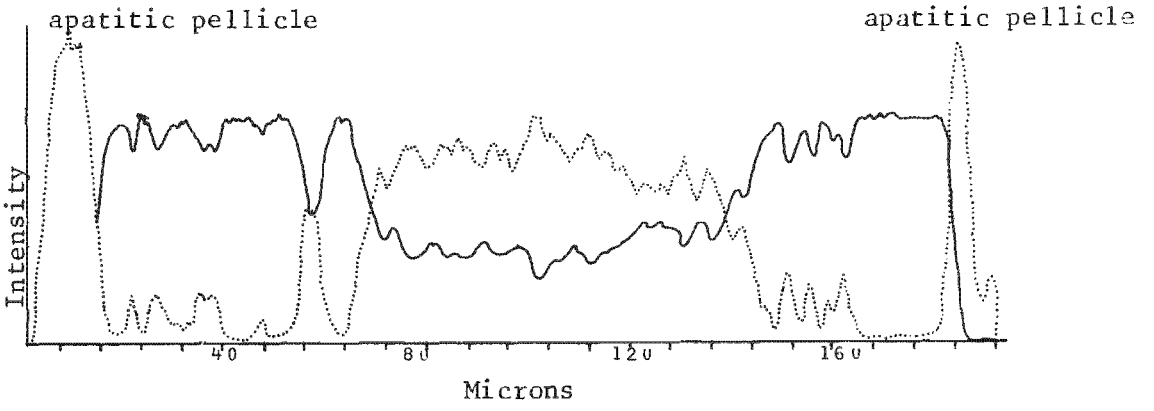
PLATE IV - 10

Plate IV-10. A phospho-glauconite pellet exhibiting a glauconitic outer margin

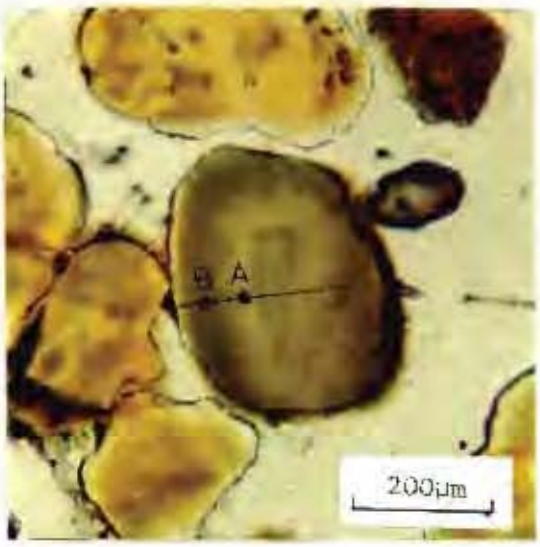
Altered grains predominantly exhibit a glauconitized outer margin. Note the apatitic pellicle and the compositional changes from the centre to the rim of the grain presented in the micro-analyses and in the line scan transect below.

ANALYSES

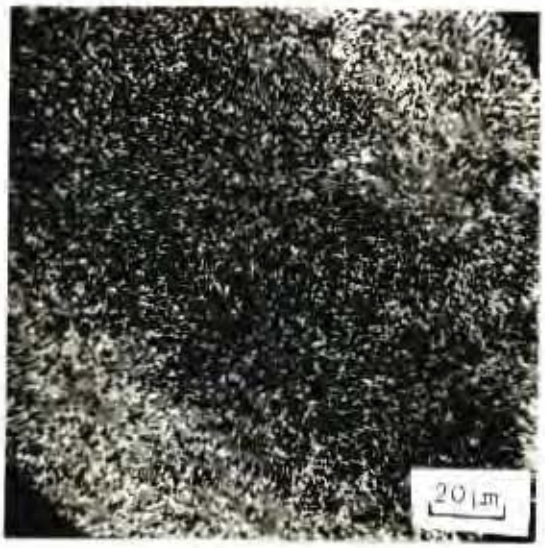
	A	B
SiO_2	16,80	46,96
Al_2O_3	1,44	5,28
Fe_2O_3	9,84	23,08
MgO	1,50	3,98
CaO	36,56	3,16
Na_2O	0,37	0,13
K_2O	3,15	8,63
P_2O_5	23,29	1,95
Total	92,95	93,17



LINE SCAN OF Ca (····) and Si (——)



Photomicrograph



Fe

P

K

Ca

Si

Plate IV-10

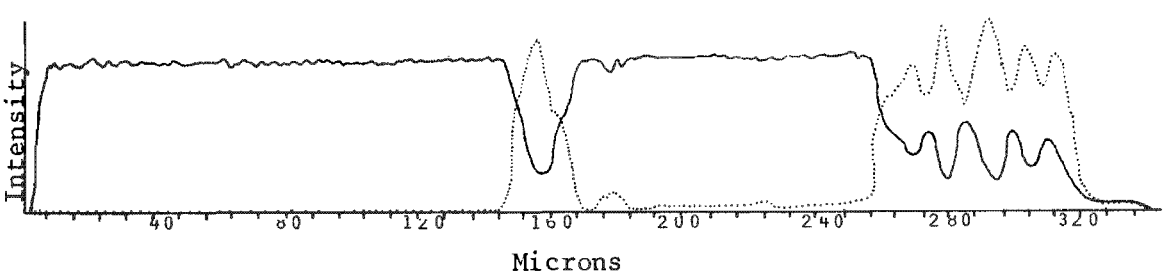
PLATE IV - 11

Plate IV-11. A coarsely mottled phospho-glauconite grain

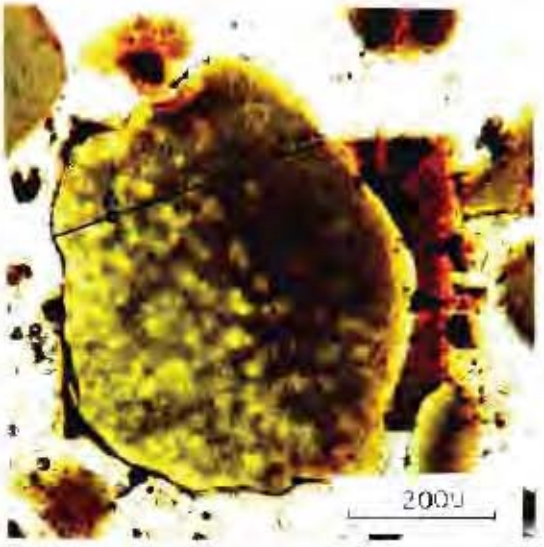
Segregations of apatite, 20-50μm in size, are randomly dispersed through the grain presented on the opposite page. The variation in composition can be judged by the line scan across the pellet and by the two accompanying micro-analyses.

ANALYSES

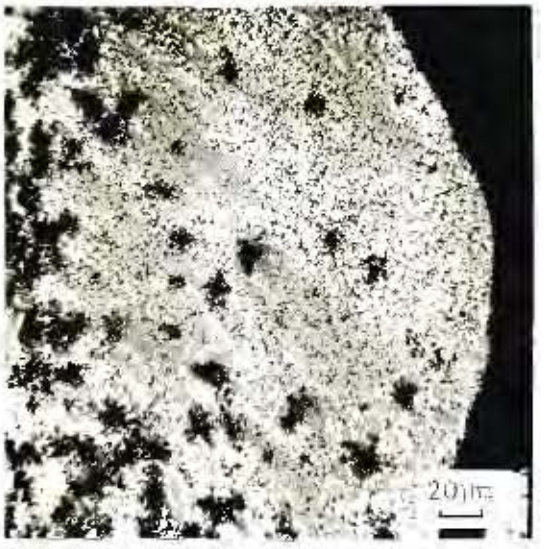
	A	B
SiO_2	24,08	47,11
Al_2O_3	2,48	5,48
Fe_2O_3	10,69	19,13
MgO	2,38	4,72
CaO	29,66	5,46
Na_2O	0,49	0,13
K_2O	4,23	7,90
P_2O_5	19,24	3,52
Total	93,25	93,45



LINE SCAN OF Ca ('''') AND Si (——)



Photomicrograph



Fe

P

K

Ca

Si

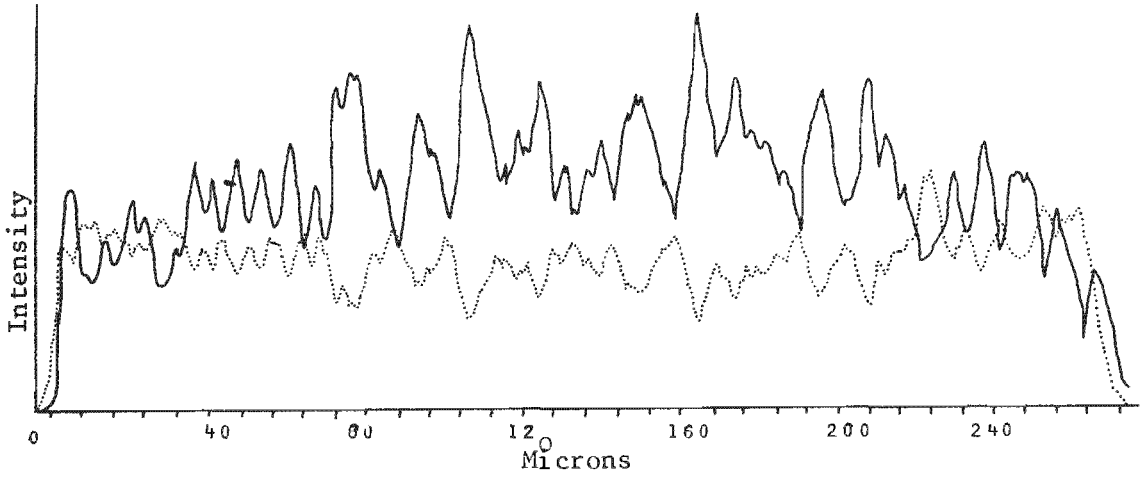
PLATE IV - 12

Plate IV-12. A finely variegated glauco-phosphate pellet

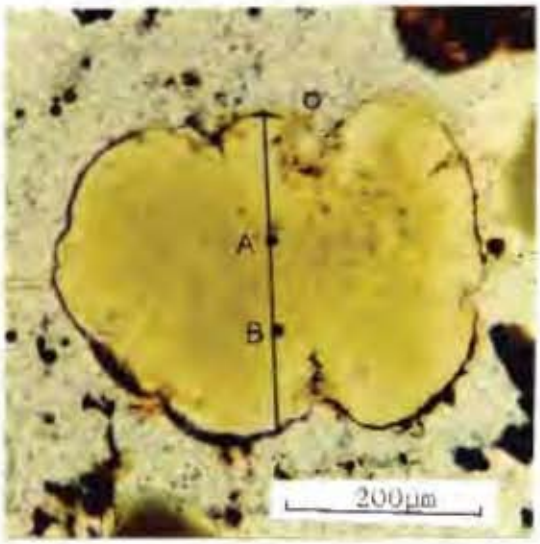
Variegated pellets can comprise a homogeneous admixture of finely divided glauconite and apatite. At high magnifications (X2500) a general patchiness is apparent, but individual phases are still not resolved. The general heterogeneity of the material can be seen below in the micro-analyses and in the line scan across the pellet.

ANALYSES

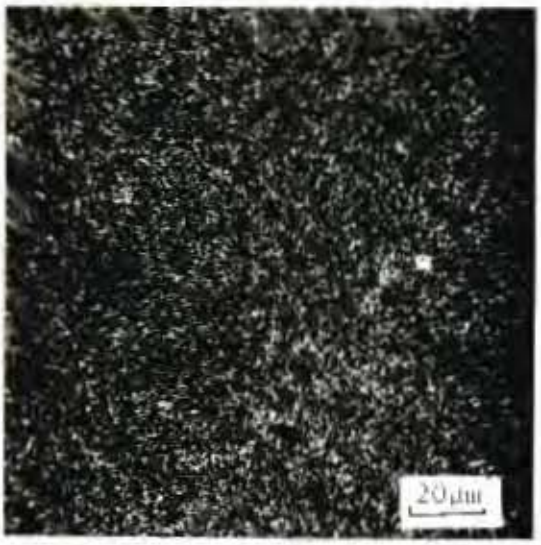
	A	B
SiO_2	21,24	18,35
Al_2O_3	3,03	2,71
Fe_2O_3	9,45	7,94
MgO	2,01	1,82
CaO	32,16	35,71
Na_2O	0,23	0,24
K_2O	3,49	2,84
P_2O_5	20,81	22,75
Total	92,42	92,36



LINE SCAN OF Ca (····) AND Si (——)



Photomicrograph



Fe

P

K

Ca

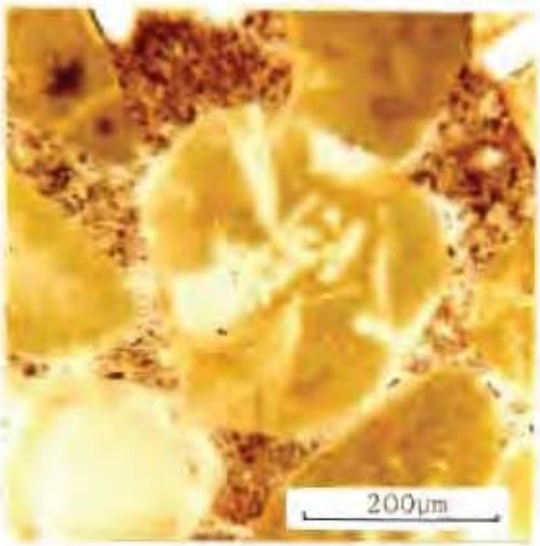
Ca(x 2500)

Plate IV-12

Plate IV-13. Internal dilation cracks in variegated pellets filled with apatitic material

Fibrous apatite radiates normal to the wall of the dilation crack in the pellet presented on the left hand side of the illustration opposite. The fibrous mineral is in turn partially lined by a granular, brownish iron-rich mineral, possibly haematite. Fractures in the variegated pellet shown on the right hand side of the illustration are entirely filled with apatite.

Photomicrograph



Photomicrograph

Ca

Ca

Fe

Si

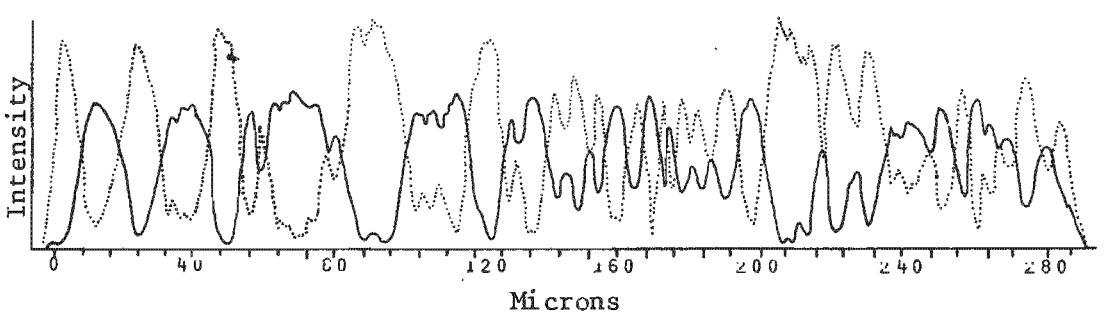
Plate IV-13

Plate IV-14. A heterogeneous grain

The heterogeneous grain shown opposite has a composition similar to that of some phosphorite matrices. The heterogeneity can be seen in the line scan reproduced below.

ANALYSIS A

SiO_2	7,50
Al_2O_3	1,42
Fe_2O_3	3,88
MgO	1,21
CaO	46,58
Na_2O	1,02
K_2O	1,51
P_2O_5	28,91
Total	92,03



LINE SCAN OF Ca (····) AND Si (____)

Photomicrograph

Fe

P

K

Ca

Si

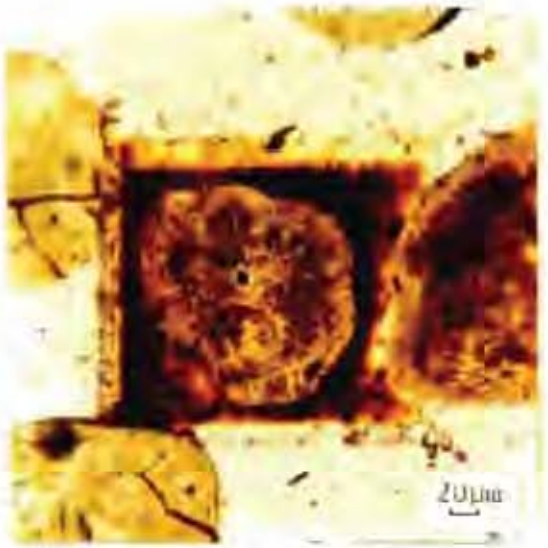
PLATE IV - 15

Plate IV-15. An immature glauco-phosphate pellet

The pellet shown apposite consists of an evenly distributed admixture of finely divided glauconite and apatite, whereas the foraminiferal test enclosed in the pellet is filled with pure glauconite. Most variegated pellets are composed of mature glauconite. However, immature glauconite also contains phosphatic inclusions as shown in this figure. This implies that the apatite phase is present at the earliest stage of pellet formation.

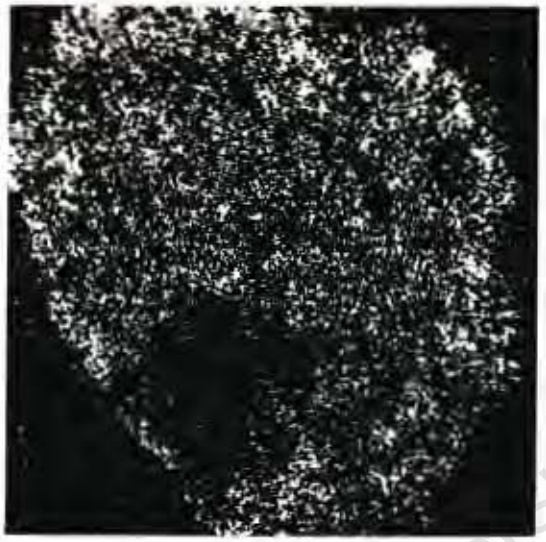
ANALYSIS A

SiO_2	32,49
Al_2O_3	3,92
Fe_2O_3	12,35
MgO	4,15
CaO	17,77
Na_2O	0,67
K_2O	5,68
P_2O_5	11,99
Total	89,02



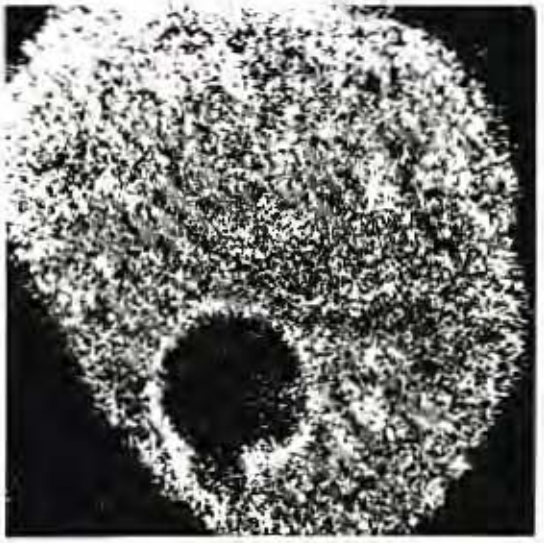
Photomicrograph

Fe



P

K



Ca

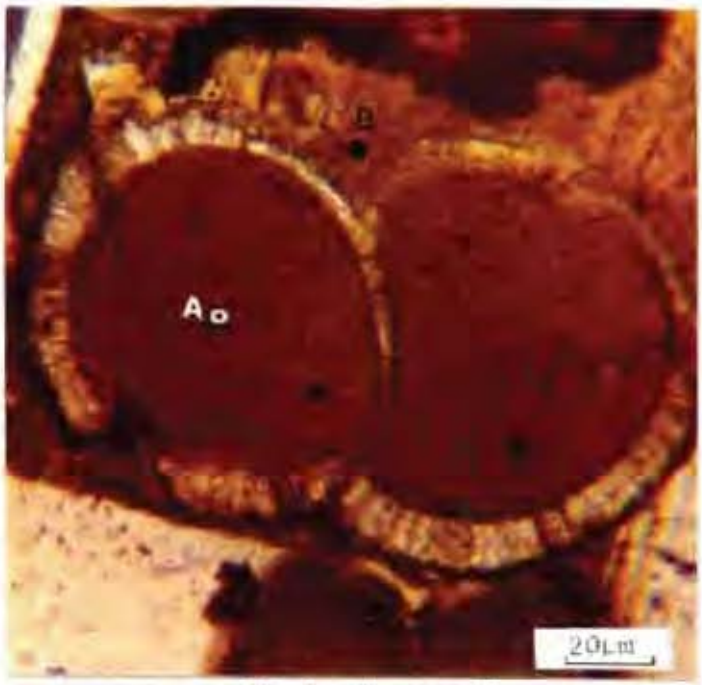
Si

Plate IV-16. A foraminiferal test containing a homogeneous mixture of glauconite and apatite

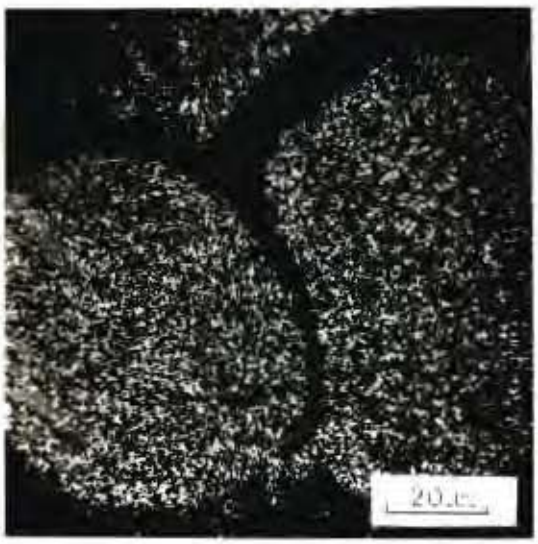
The foraminiferal test shown opposite is filled with a finely (<1μm size particles) disseminated mixture of glauconite and apatite. Note that the calcite shell is unaltered and that the fill material is similar in composition to the ambient phosphorite matrix.

ANALYSES

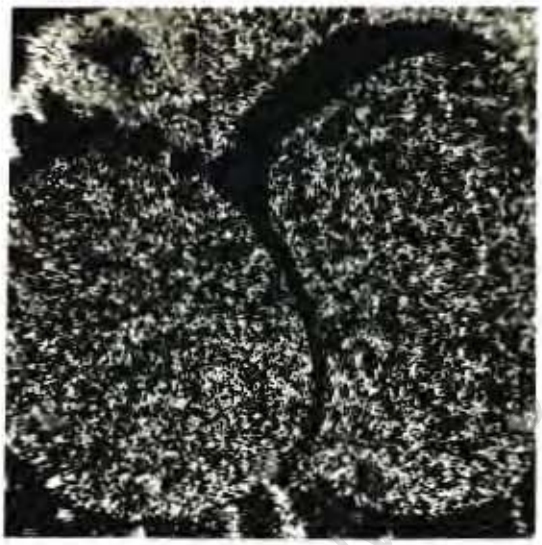
	A	B
SiO_2	16,48	15,51
Al_2O_3	1,89	1,78
Fe_2O_3	10,37	10,11
MgO	2,31	2,29
CaO	32,29	33,01
Na_2O	0,89	0,93
K_2O	2,91	2,89
P_2O_5	20,44	21,31
Total	87,58	87,83



Photomicrograph



Fe



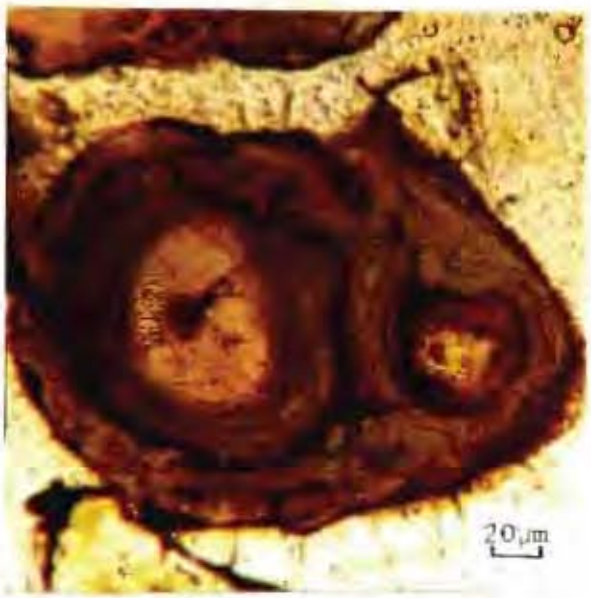
P

K

Ca

Si

Plate IV-16



Photomicrograph

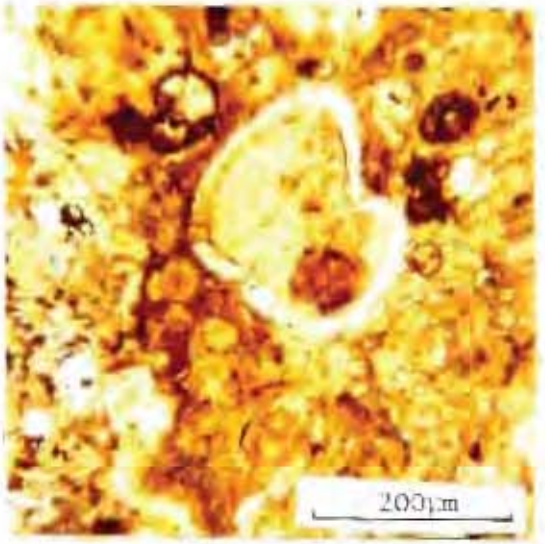
Fe

P

K

Ca

Si



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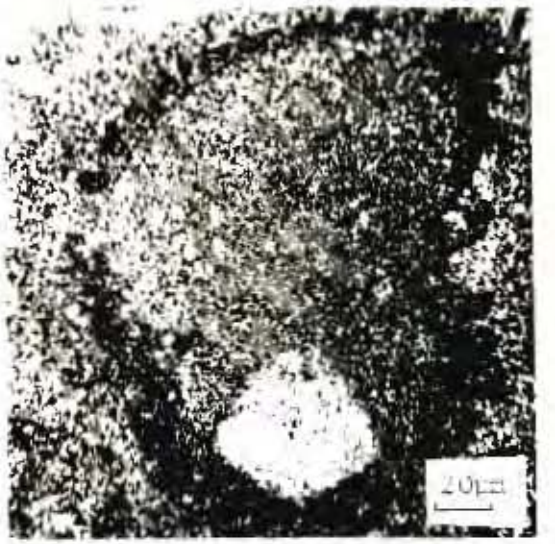
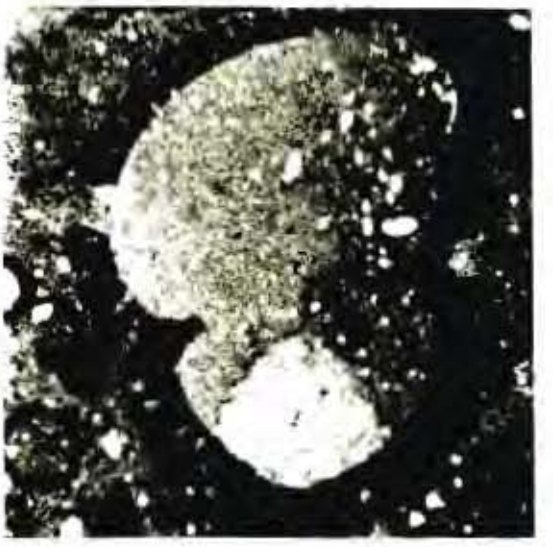


Fe

P

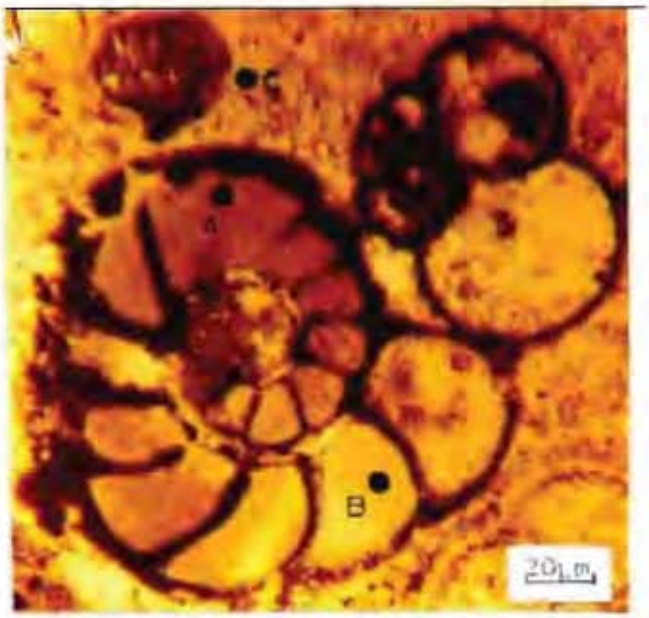
K

Ca

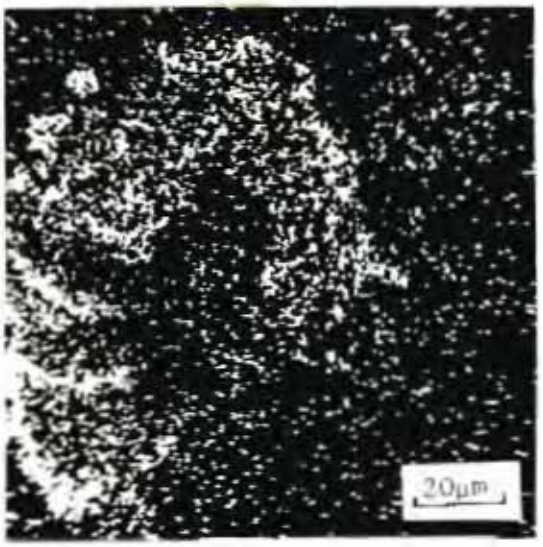


Si

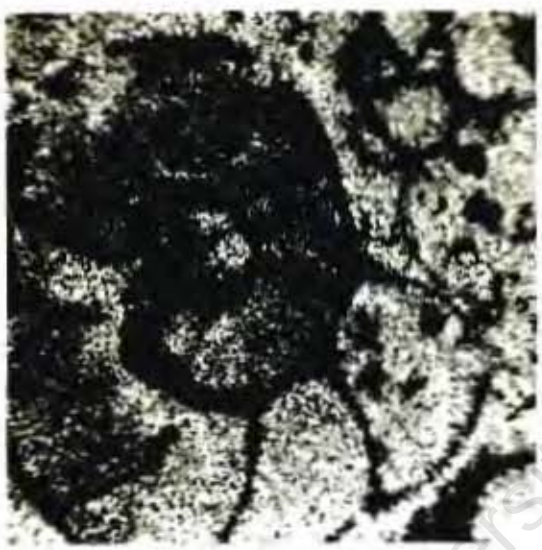
Plate IV-18



Photomicrograph



Fe



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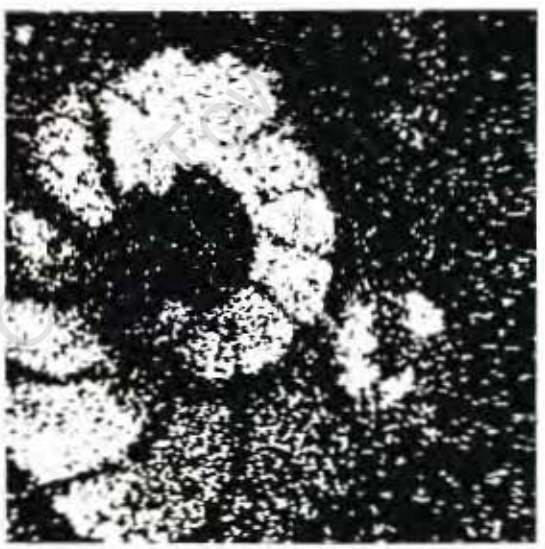


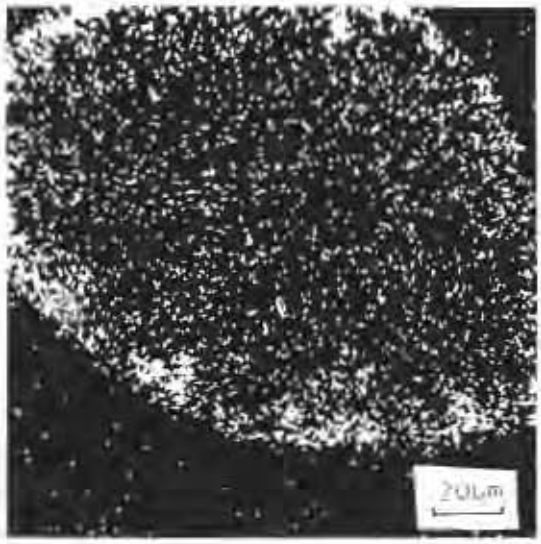
K

Ca

Si

PLATE IV - 20

Photomicrograph



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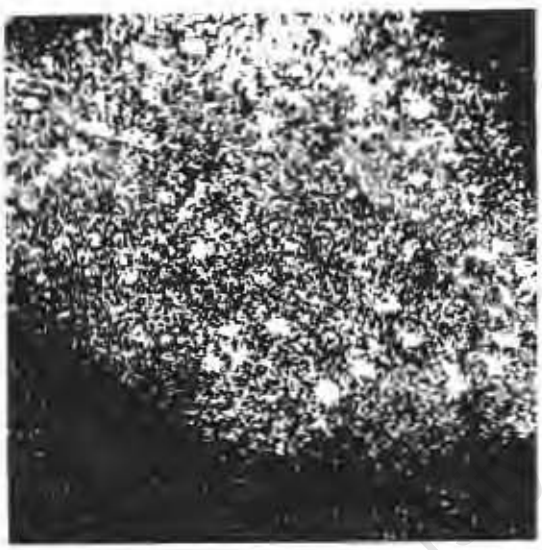

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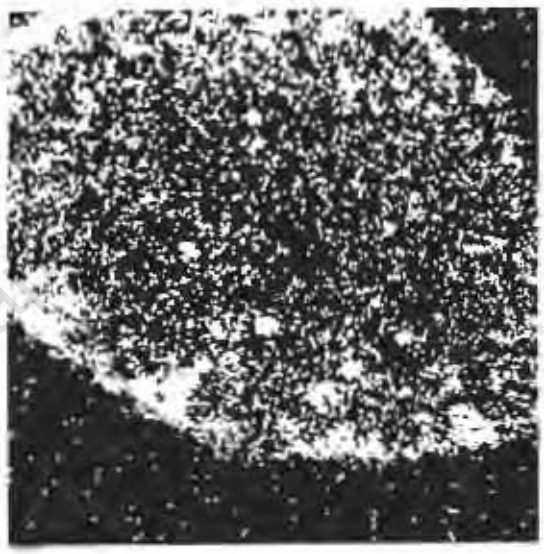

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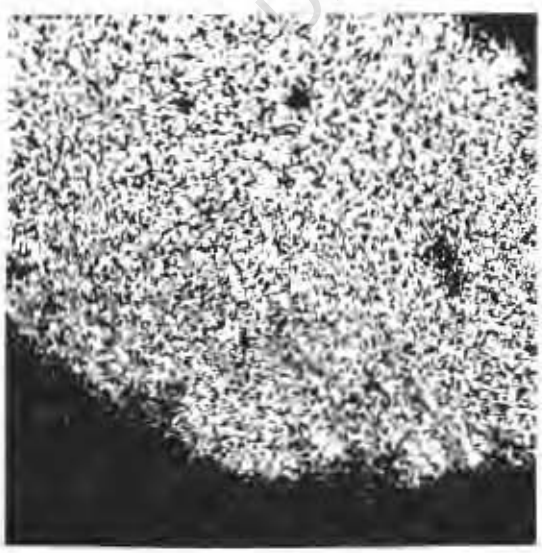

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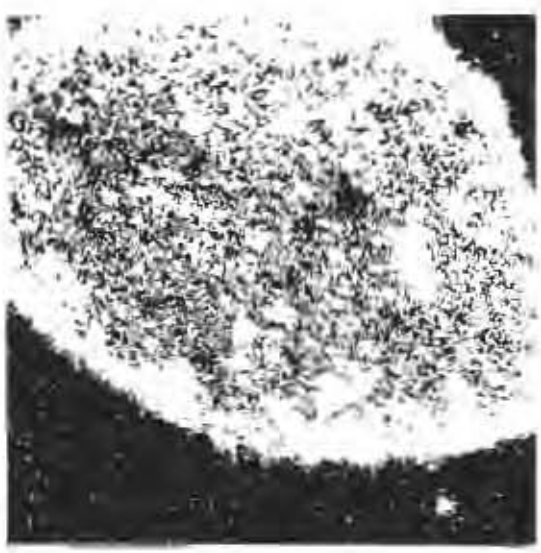

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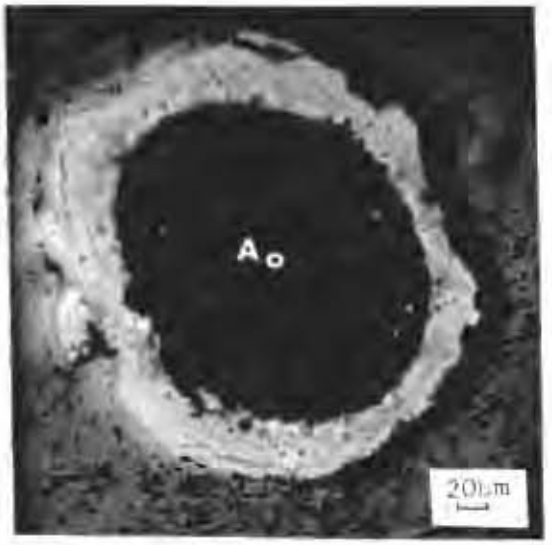

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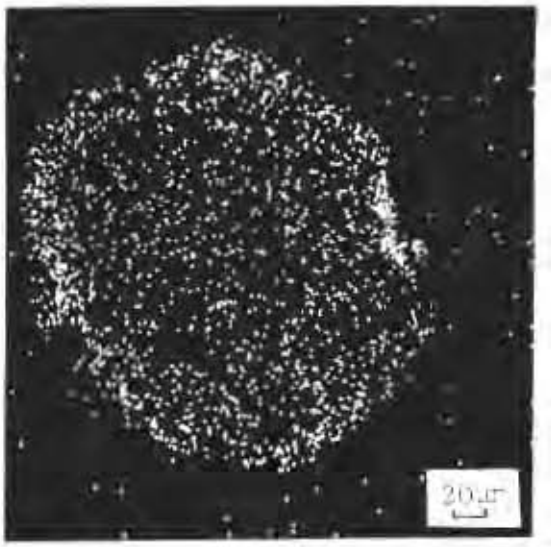

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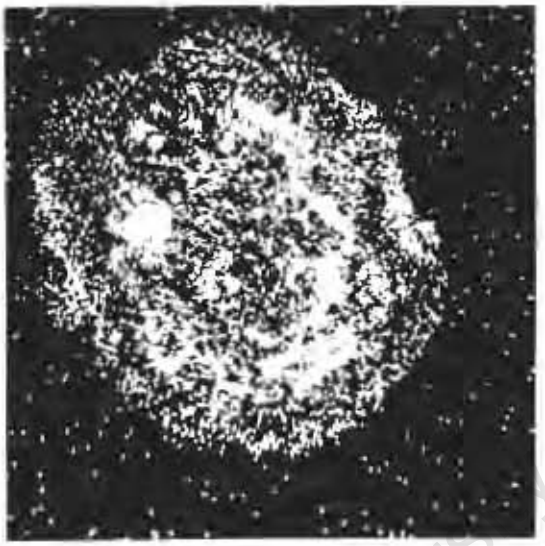

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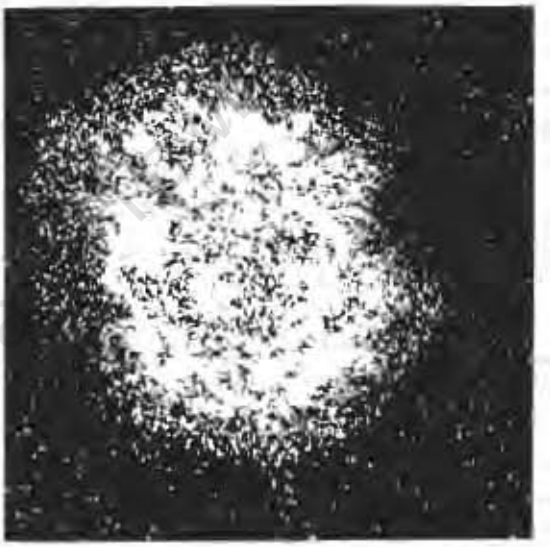

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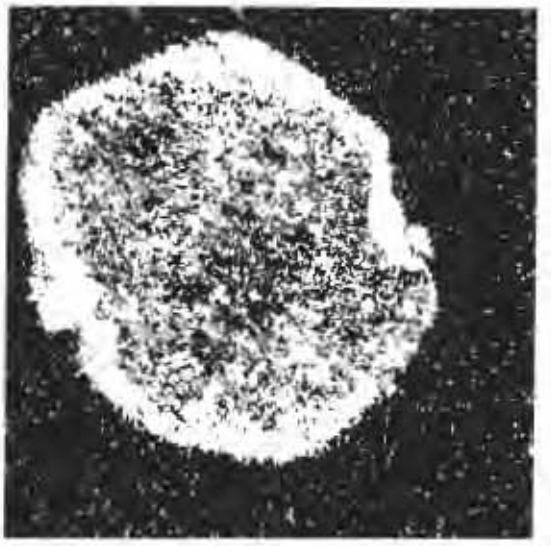

Si

A

B

C

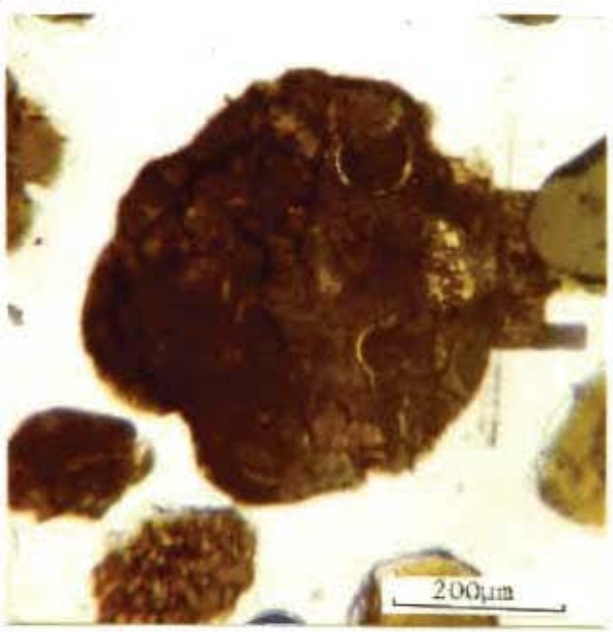

Figure I-1